Growth and Characterization of
CrB$_2$/TiB$_2$ Superlattices by Magnetron
Sputtering

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Abstract

In the present work, growth and structural characterization of CrB₂/TiB₂ superlattices on (0001) Al₂O₃ substrate is studied. The superlattices are grown using a direct current magnetron sputtering (DCMS) system with a base pressure of < 9E-7 Torr.

For structural characterization X-ray diffraction (XRD), X-ray reflectivity (XRR), transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive X-ray spectroscopy (EDX), and scanning transmission electron microscopy (STEM) are used. Hardness is measured using nanoindentation technique.

For growth of CrB₂/TiB₂ superlattices it is shown that the sputtering gas pressure of Pₘₐₚ= 4 mTorr, and substrate temperature of T= 600 °C are optimized parameters for growing well-structured superlattices with good interface quality. Superlattices with a layer thickness ratio of Γ= 0.43 (Γ= Dₚ/TiB₂/Dₘ₂/TiB₂) and a total thickness of 1 µm are deposited with different modulation periods Λ=1, 2, 6, 8, and 10 nm to see the layer-thickness affect on the quality of the structures. XRD and TEM results show that by increasing the modulation period, the quality of superlattices with smooth interfaces increases. The superlattices with modulation period Λ=8 nm is shown to be the best structure having coherent lattice and smooth interfaces up to ~20 periods. The STEM analysis shows that after about 20 periods, grains started to grow at slightly different orientations. A superlattice of TiB₂/CrB₂ (having TiB₂ as the first deposited layer) with modulation period Λ=8 nm shows an epitaxial growth of TiB₂ on Al₂O₃ (0001) substrate, however, no big difference between the structure of TiB₂/CrB₂ and CrB₂/TiB₂ superlattices is seen.

EDX maps and line profiles show that there is a diffusion of CrB₂ into TiB₂ layers which is a serious problem for obtaining sharp interfaces. STEM also shows that for a small modulation period of Λ=1 nm, there is a faint layered structure, whereas EDX, SAED and XRD indicates a homogenous textures Ti-Cr-B film in this sample.

Finally, the hardness measurement shows a hardness value of 29-34 GPa for different modulation periods. The lowest hardness value is related to the sample with modulation period of Λ=1 nm with about 29 GPa, and the highest hardness is related to the sample with Λ=8 nm with around 34 GPa.
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My contribution

I started this study by reading relevant articles to the field. Because of doing other projects before the start of this work and using the same equipment, for this study I could do all the experimental parts by myself. At the beginning of the work, with the help of my supervisor I could plan the depositions and parameter optimizations. I did 34 depositions on total, and 7 depositions took more than 6 hours each.

The characterization part including X-ray diffraction and X-ray reflectivity of the samples was done by myself. Preparing TEM samples was also done by myself.

Another contribution that I had for my project was analyzing the data.

The structure of the report and the content are written by me (I read some PhD thesis and got the idea of the general structure for an academic report).

All schematic figures in the report (except two of them that have references) are created by me. All the graphs and images in the report are the result of my own experiments which are plotted by myself.
Objectives

The main objective of this study is to demonstrate the growth possibility of CrB$_2$/TiB$_2$ superlattices by magnetron sputtering. After being able to grow these superlattices, they should be characterized by different techniques such as X-ray diffraction (XRD), X-ray reflectivity (XRR), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDX), and hardness by nanoindentation.
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1. Introduction

Transition metal nitrides such as e.g. CrN, ZrN, and TaN superlattices and multilayers at nanometer scales have been popular and widely used due to their superhardening effect [1]. For the compositional modulation period, $\Lambda$, in the nm range, a hardness enhancement up to 2.5 times more than the individual constituents have been reported [2]. Such materials are used as hard coatings on cutting tools with a high wear resistance at high temperatures [1,3]. While many studies have been mostly focused on controlling the composition of these films and also enhancing their mechanical properties, there seems to be few investigation on growing TM diboride superlattices with high reflectivity properties suitable for neutron mirrors.

This thesis is focused on growth and characterization of CrB$_2$/TiB$_2$ superlattices on (0001) Al$_2$O$_3$ substrate. In the following section, the structure of CrB$_2$ and TiB$_2$ which constitute the superlattices in this study will be discussed.

1.1 Structure of TiB$_2$ and CrB$_2$

Early transition metal (TM) diborides are ceramic materials that show high hardness values, high melting points, and good wear and corrosion resistance. They crystallize in the so-called AlB$_2$ structure type with space group 191 (P6/mmm) and three atoms per hexagonal unit cell. Fig. 1 shows an instructive description of this structure as a stacking of hexagonal planes of covalently bonded boron atoms, separated by the metal layers. The boron atoms crystallize graphite-like, covalently bonded hexagons, having metal atoms below and above their centers [4-6].
TiB\textsubscript{2} is one of the popular transition metal diborides due to properties such as high hardness (for bulk about 24 GPa), high melting point (3500 K), high thermal and electrical conductivity, high strength, and excellent chemical stability at elevated temperature. TiB\textsubscript{2} is used in many applications such as coatings on engine components in aerospace because of its low density and high thermal conductivity. TiB\textsubscript{2} crystallizes in the hexagonal AlB\textsubscript{2} type structure, where boron atoms are placed in interstitial positions between close-packed Ti planes along c direction. It is synthesized using different techniques such as chemical vapor deposition and arc deposition although the most commonly used technique is magnetron sputtering [6-11].

On the other hand, CrB\textsubscript{2} coatings also exhibit good properties such as high melting point (about 2470 K), high hardness (for bulk between 11-20 GPa), good chemical stability at elevated temperature, corrosion resistant, lower electrical contact resistance, and excellent optical properties which make them a good candidate for wear resistant, anti-corrosion, electrical contact solar, and selective absorber applications [12,13]. The structure of CrB\textsubscript{2} is AlB\textsubscript{2}, the same as other early transition metal diborides which is discussed above.

1.2. Superlattices

Superlattices can be categorized in the family of multilayers. When there is a coherent modulation along the growth direction in addition to coherent interfaces and very thin layers at nano meter scale in a multilayer sample, it is called superlattice. In the growth direction, in addition to the interatomic distances (d\textsubscript{A}, d\textsubscript{B}), another parameter which is called the modulation period \( \Lambda = D_A+D_B \) is used when talking about superlattices [14-16]. Fig. 2 shows a schematic view of a superlattice with different layer thicknesses. In the X-ray diffraction pattern related to a superlattice, a central Bragg peak will be flanked by some peaks which are called satellite peaks. The average lattice spacing in a superlattice can be calculated from the position of the central peak. The appearance of higher order satellites with higher intensities shows a sharper types of modulation in the superlattice.
To control the individual layer thicknesses and the interface sharpness, parameters such as; the deposition rates, the rate fluctuations and the shutter or rotation speeds are important and should be considered. However, the sharpness of each individual layer interface can also be determined by the thermodynamics of the material system. For example, some degree of interdiffusion can be expected in a case that two materials are soluble in each other while in a case of totally immiscible elements, one can expect sharp interfaces or an interfacial compound [17]. When the lattice parameters of constituents are different, the sharpness of interfaces can be affected by the strain, e.g changing the growth mode from a layer-by-layer growth to a three-dimensional island growth. Different growth modes are explained in the following section.

2. Growth mechanisms

Thin film formation on a substrate in various vapor deposition techniques can be categorized into three main steps; (i) production of a vapor phase (atomic, molecular, or ionic species), (ii) transportation of the vapor species to substrate surface, and (iii) condensation on the substrate and film nucleation and growth [18,19]. The properties of thin films formed by vapor deposition processes largely depend on these steps.
2.1 Nucleation and growth of thin films

Understanding nucleation and growth at the atomic scale is essential for thin films. The main deposition variables which obtain nucleation and growth kinetics, microstructural evolution, and thus, films properties are film material, flux and kinetic energy of species incident at the growing surface, growth temperature, contaminants, and the substrate material, surface cleanliness, crystallinity, and orientation [20]. Thin films growth usually follow five main stages; (i) stable cluster nucleation, (ii) island growth, (iii) island coalescence, (iv) polycrystalline island formation, and (v) continuous film growth [21]. Adsorbed atoms (adatoms) diffuse on the surface, controlled by material atomic bonding, substrate temperature, and adatoms kinetic energy, until they either reach a critical size and form stable nuclei or desorb. The stable nuclei then grow, by incorporation of more adatoms and sub-critical clusters, and form islands. Then, the islands coalesce with their neighbours, which results in a decrease in island density, and eventually, continuous film grows by continuing deposition process.

Initial growth stages, depending on thermodynamic conditions and substrate surface, can be categorized as (i) island growth (Volmer-Weber), (b) layer-by-layer growth (Frank-van der Merwe), and (c) mixed growth (Stranski-Krastanov). The nucleation and different growth modes are schematically represented in Fig. 3. It is worth mentioning there are some growth conditions that follow none of these three growth models, like reactive intermixing [19-22].

Fig. 3. Schematic of (a) nucleation and (b) growth modes.
2.2 Growth techniques

Synthesis techniques of vapor-based thin films are divided into two groups; chemical vapor deposition (CVD) and physical vapor deposition (PVD).

In the PVD process, a solid surface, target, is impinged with energetic particles, typically accelerated ions, and near surface atoms are removed and ejected from the solid surface. This phenomenon is called sputtering and is illustrated in Fig. 4. The sputtered target atoms then travel through the chamber and condense on the substrate. In principle, energetic incident particles colliding the solid atoms transfer their energy to the atomic nuclei. When the transferred energy is sufficiently high to overcome the binding energy at the lattice site, a primary recoil atom is produced. The kinetic energy of the sputter-ejected particles, 5-25 eV, is substantially greater than evaporated particles. A significant number of the sputtered particles are neutral. In addition to sputtering, bombarding a solid with high energetic particles can cause backscattering, which is really pronounced when the mass difference between target material and bombarding gas atoms is negligible, local heating, implantation, desorption of surface layers, electron and photon emissions, and a change in surface structure and topography, which appears as an eroded region at target surface, called race track [20, 23, 24], occurs.

Sputtering can be measured by sputtering yield $S$ which is the average number of sputtered atoms from a solid surface per incident particle, and depends on energy, mass, and angle of

![Fig. 4. Schematic of physical sputtering process.](image-url)
incident particles, as well as crystallinity, crystal orientation, surface binding energies, and mass of target atoms [20, 23, 24].

In sputtering deposition, target is mounted opposite the substrate in a chamber and then, the chamber is evacuated to a desired pressure, ranging from $10^{-6}$ to $10^{-10}$ Torr depending on the process. Thereafter, the evacuated chamber is filled with a continuous flow of a gas, typically Ar, required for producing a discharge and providing the ion bombardment necessary for sputtering. A discharge is an ionized atmosphere which usually contains ions, electrons, and un-ionized particles. The discharge is ignited by applying a negative potential to the target, mostly direct current (DC) or radio frequency (RF), depending on target materials. This process is called diode sputtering. In an electric field, a free electron is rapidly accelerated from the cathode, which is target in sputtering process, toward the anode. The electron can gain sufficient energy to collide and ionize gas atoms, depending on gas pressure. When the energy of this electron is higher than the energy required for the ionization of gas atoms, the electron-gas atom collision can ionize the gas atom and create one additional electron, which is called secondary electron, $(e^- + Ar \rightarrow Ar^+ + 2e^-)$. These secondary electrons are responsible for sustaining the discharge. When a positive gas ion collides with a gas atom in the discharge, they can either exchange momentum and energy or charge. For example, fast ions colliding with slow neutrals can extract an electron from the slow neutral and then, the fast ion becomes a fast neutral, while the slow neutral becomes a slow positive ion. Generally, DC-diode sputtering is relatively slow compared to other PVD processes, due to the relatively low electron density around the target, and needs high gas pressure [20, 24].

### 2.3 Magnetron sputter deposition

In order to deal with the low deposition rate of DC-diode sputtering, a magnet can be used behind the target to confine free electrons in target surface vicinity, increase ionization, and enhance sputtering. This process is called magnetron sputtering (see Fig. 5). A magnetic field can significantly influence on the movement of charged particles. The force applied to a charged particle $q$ with $\vec{v}$ velocity by a $B$ magnetic field is $q\vec{v} \times B$. If the charged particle moves at right angles in the magnetic field, this force causes the particle to move in an orbital path. The orbit radius can be shown in terms of particle kinetic energy, $KE$, and its mass, $m$, as $\sqrt{2m \times KE} / qB$. The movement of a charged particle is affected in a magnetic field only if its moving orientation is perpendicular to the magnetic field. A magnetic field can accelerate the velocity of a charged
particle only if the electric field is perpendicular to the magnetic field, which is known as $E \times B$ drift. Based on the orbit equation, charged particles with either high energy or high mass have large orbits. The orbit radius of ions is significantly larger than that of electrons, as the mass of ions is higher than electrons, and also the orbit of ions is larger than the chamber size; hence, the effect of magnetic field on ions can be ignored. In order to achieve even higher levels of ionization or guide the discharge toward the substrate, most of magnetrons are unbalanced, either inner or outer pole is more powerful than the other one. The primary advantages of magnetron systems are high deposition rates, low sputtering pressures, low substrate temperatures, and the ease of conversion to industrial scale. However, the maximum deposition rate in magnetron sputtering process is limited by the cooling ability of target because applying high powers (potentials) cause target overheating and melting [24].

The sputtering system used for the synthesis of CrB$_2$/TiB$_2$ superlattices presented in this work is a dual target sputtering system with a cylindrical chamber (500 mm diameter and 350 mm height). The distance between the target and substrate is 120 mm. Fig. 6 shows the schematic view of the system. Two, 75-mm-diameter, magnetrons are positioned in the top plate of the vacuum chamber, each with a tilt angle of $25^\circ$ with respect to the substrate surface normal. In order to deposit CrB$_2$ and TiB$_2$ sequentially, computer controlled shutters in front of each targets are used which have a high accuracy of a fraction of second and allow the system to obtain the desired layer thicknesses together with fairly low deposition rates. More details regarding the deposition system can be found e.g. [15, 26, 27].

Fig. 5. A planar magnetron with a disk target [25].
2.4 Ion-assisted sputter deposition

In most applications it would be desirable to have abrupt and flat interfaces for multilayers and superlattices of course. One option could be the substrate rotation during deposition to improve the thickness uniformity of different layers, but it would not be enough to ensure flat surfaces. As it is explained in the “Growth section”, the energies of atoms arriving at the substrate are not sufficient to provide enough surface mobility to grow a smooth surface and as a result there would be surface roughness on an atomic scale. One solution could be increasing the surface mobility of the atoms in the growing film which can be achieved by applying a negative bias to the substrate. In order to avoid re-sputtering and intermixing of different layers during the so called “Ion-assisted sputter deposition” the ion bombardment of the substrate has to be done at lower energies compared to the bombardment of the target. This concept is explained more in e.g [28].

In order to improve the results of ion-assisted sputtering the flux of the ions hitting the substrate has to be increased to ensure enough surface mobility of the atoms in the growing film. This could be done by having a solenoid around the substrate which generates a magnetic field...
axially through the substrate position. By selecting the correct direction of the solenoid current the secondary electrons of the target with the opened shutter can be guided towards the substrate. This process ensures a high ionization rate in this region and increases the ion flux that reaches the substrate, and can be seen in the deposition flux which is a purple (in case of Ar gas) plasma glow, see Fig. 7.

![Deposition flux from the target on the right side to the substrate when applying solenoid current.](image)

**Fig. 7.** Deposition flux from the target on the right side to the substrate when applying solenoid current.

### 3. Characterization techniques of superlattices

Structural characterization of multilayers are mostly done by using a combination of X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques.

#### 3.1 X-ray analyses

3.1.1 X-ray diffraction

One of the most utilized characterization techniques in materials science is X-ray diffraction. When a crystal is irradiated with X-rays, constructive interference of elastically scattered X-rays by electrons of atoms in the sample occurs based on the Bragg’s law

\[ n\lambda = 2d_{hkl}\sin\theta \]  \hspace{1cm} (1)
where \( n \) is an integer called the order of diffraction, \( \lambda \) is the wavelength of the X-rays, \( d_{hkl} \) is the distance between the lattice planes, and \( \theta \) is the diffraction angle. In fact, the minimum requirement for occurrence of the constructive interference is that the path difference between the diffracted beams is an integer of the wavelength of the coming X-rays. A schematic illustration of Bragg’s law is in Fig. 8.

![Fig. 8. Schematic illustration of Bragg’s law.](image)

However, Bragg’s law is not enough for having a reflection peak, and the allowed reflections are determined by the structure factor. The structure factor is determined by the crystal structure, and the position of the peaks in a diffractogram show which atoms are present in the crystal and where they are located, giving each material its own “fingerprint” diffractogram. Thus, XRD is a good way to confirm the identity of a material, and also the crystal quality, lattice parameter and, the orientation of the film.

The method which is used in the present work is a so called \( \theta/2\theta \) scan. The \( \theta/2\theta \) scan is a symmetrical scan in which the incident and reflected angle are always the same, and thus, only the crystal planes parallel to the sample surface will be seen in the diffraction pattern. In thin films it is common that some of the growth directions are more favorable than others and have more probability of being parallel to the surface. The very high intensity of a diffraction peak compare to the other peaks might show that the film is either textured or epitaxial. \( 0-20 \) x-ray diffraction (XRD) scans at this thesis are carried out using a Philips X’Pert X-ray diffractometer with a Cu-K\( _\alpha \) source (\( \lambda = 1.5406 \) Å).
3.1.2 X-ray reflectivity

By using X-ray reflectivity (XRR) which is ideally suited for investigation and characterization of thin films and multilayers, several parameters such as the period (Λ) or the thickness of individual layers, and interface width can be obtained. In this method the diffractometer is operated in the symmetric θ/2θ configuration, using much smaller angles compared to those in θ/2θ diffraction. A schematic view of reflectivity from a typical multilayer used for X-ray mirrors is shown in Fig. 9.

![Schematic illustration of a multilayer reflectivity used for X-ray mirrors.](image)

Fig. 9. Schematic illustration of a multilayer reflectivity used for X-ray mirrors.

The reflectivity of each individual interface is related to different parameters such as the difference in density across the interface, the angle of incidence (θ), and the wavelength of the incident X-rays (λ). When θ is adjusted to the right angle for a specific wavelength, the reflected beams are in-phase. Modified Bragg’s law, which relates the distance between the reflecting planes (Λ) to θ and λ, corrected for the refractive index η for X-rays, can be used here.

\[ \eta = 1 - \delta - ik \tag{2} \]

Where δ and k are usually small positive numbers which can be calculated to be in the range 0.005 to 0.5 for soft X-rays depending on λ and the material used. The modified Bragg’s law is

\[ n\lambda = 2\Lambda \sin\theta \sqrt{1 + \frac{\eta^2 - 1}{\sin^2 2\theta}} \tag{3} \]
In the equation above, n is the order of the reflection. For such application, it is important to have high structural interlayer, lateral and chemical order. In order to achieve as coherent scattered X-rays as possible, the interfaces must be as flat as possible, the layer thicknesses may not fluctuate and the microscopic roughness must be minimized in these structures. The local interfacial difference in Z decreases with decreased reflectivity due to the interdiffusion at the interfaces which makes them wider [15].

3.2 Electron microscopy

3.2.1 High resolution transmission electron microscopy

In transmitted electron microscopy (HRTEM), electrons are accelerated to a voltage of about 200 keV and then either transmitted through or scattered from the sample which results in different intensities of the transmitted beam holding information of the structure of the sample. TEM requires the sample to be very thin, preferably less than 50 nm thick. In high resolution transmission electron microscopy (HRTEM) phase contrast is obtained. Transmitted and scattered beams both are used and the path difference of the two beams gives rise to interference and therefore generates contrast in the image. It is possible to get lattice resolved images using HRTEM. TEM microscope that is used for this study is FEI Tecnai G2 TF20 U-Twin, operated at 200 kV.

3.2.2 TEM sample preparation

TEM sample preparation is complicated and time-consuming as well as destructive. In the first step, for a cross-sectional sample, two pieces of size 1×1.8 mm² are cut out of the sample and placed in a 1 mm titanium grid while the films are facing each other. This step is followed by polishing both sides with diamond paper 30, 15, 6, 3, and 1 to reach a thickness of around 50 µm. The final step which is thinning the sample to an electron transparent stage is done by low angle ion milling. TEM sample preparation at present work was done by mechanical polishing and grinding followed by ion milling using a Gatan PIPS with sample rotation, at 5 keV and a 6° incident angle on both sides of samples. During the final stages of sample thinning, the ion energy is reduced to 1.5 keV.

3.2.3 Selected Area Electron Diffraction

In a TEM a diffraction pattern is formed in the back focal plane of the objective lens when Bragg’s law is fulfilled in a similar way as in XRD. The diffraction pattern can be imaged
instead of the ordinary image by changing the strength of the intermediate lens. An aperture inserted in the image plane of the objective lens which makes it possible to choose a beam from a very limited part of the sample, the so called Selected Area Electron Diffraction (SAED), and therefore obtain crystallographic information from a very small area of interest.

3.2.4 Bright field and Dark field
Two commonly used TEM imaging modes are bright field (BF) and dark field (DF). In BF, an aperture in the back focal plane of the objective lens is used to block the scattered electrons and the image is constructed based on the intensity of the transmitted beam. The areas that permit more electrons to be transmitted through the sample are imaged as lighter than the areas of the sample which diffract more (darker areas). In order to use DF, the aperture in the back focal plane of the objective lens is used to block the transmitted beam, and the scattered electrons are used for imaging. The areas that diffract more will be displayed as bright.

4. Summary of the present work
4.1 Growth of CrB$_2$/TiB$_2$ superlattices
There are some important parameters which should be considered when growing thin films or multilayers such as the base pressure of the chamber, the power applied to each magnetrons, pressure of the sputtering gas, substrate bias voltage, coil current, and the duration that each shutter should be opened in case of growing multilayers and superlattices. In this study, some values are chosen to begin with. For example, current of 200 mA is applied to each magnetron, the coil current is 5 A, substrate bias voltage of -30 V, and Ar gas pressure is chosen to be 5 mTorr. But, before starting deposition, temperature calibration of the substrate needs to be done.

4.1.1 Temperature calibration
Substrate temperature calibration is done before starting the deposition. To do that, a sample of TiB$_2$ film grown on sapphire is used and the emissivity value of $\varepsilon=0.5$ is considered. A pyrometer is mounted on a window on top of the chamber, and the substrate temperature is measured from 450 to 900 °C with 25 degree intervals. An error of ±50 degree is expected, and the reason is that the pyrometer could not be focused because of the distance from the window on the chamber to the substrate is less/more than its focal point. The process of heating and measuring the temperature is repeated 6 times and the average is shown in Fig. 10.
4.1.2 Deposition rate calibration

The very first step after temperature calibration is defining the growth rate for each target material (in this case CrB$_2$ and TiB$_2$). This vital step determines how many Å/sec the layer grows during deposition, for both materials. The deposition rates can be calculated by synthesizing two periodic superlattices $i = 1, 2$ with different deposition times for each target material. Then, a set of linearly independent equations is obtained

$$\Lambda_i = t_{Ai}r_A + t_{Bi}r_B$$

(4)

from which the deposition rate for both materials (here $r_{CrB2}$ and $r_{TiB2}$) can be extracted easily.
4.1.3 Pressure optimization

Pressure of the sputtering gas is one the important parameters which can affect the growth condition. In order to optimize pressure for deposition, films are grown at three different Ar pressures (which is the sputtering gas) while other parameters such as growth temperature and number of periods are kept constant. In this work, the pressure optimization is done for two set of modulation period \( \Lambda = 2 \) and 4 nm. Fig. 11 and 12, show 0-20 X-ray diffractometers of these films. The (001) and (002) superlattice peaks are appeared at the middle of the (001) and (002) peaks of CrB\(_2\) and TiB\(_2\) (in this case because of the same thickness for both layers), and are called the common peaks. For films with \( \Lambda = 2 \) nm the satellite peaks have slightly higher intensity when the sputtering gas pressure is 4 mTorr (satellite peaks and common peaks are the result of the multiplication of the structure factors of constituents). This is also the case when comparing different pressures for films deposited with \( \Lambda = 4 \) nm in which the satellite peaks corresponding to \( P_{Ar} = 4 \) mTorr are narrower and sharper. Results in Fig. 11 and 12 show that 4 mTorr is optimum pressure for the superlattices.

Fig. 11. Pressure optimization for superlattices with modulation period \( \Lambda = 2 \) nm and thickness ratio \( \Gamma = 0.5 \).

T=400°C, N=30, d1,d2=1nm
Fig. 12. Pressure optimization for superlattices with modulation period $\Lambda=4$ nm and thickness ratio $\Gamma=0.5$.

4.1.4 Temperature optimization

Growth temperature is also an important parameter when growing superlattices. At high temperature atoms gain enough energy to find their best position in the lattice and form a perfect crystal. So, it is vital to find the best temperature when depositing superlattices. More information about the growth mechanisms is in “Nucleation and growth” part.

A series of superlattices at different temperatures from 400 °C to 800 °C with 100 °C intervals are deposited while the number of periods, sputtering gas pressure, and modulation period are kept the same for all of them. Fig. 13 illustrates the effect of temperature on growth of CrB$_2$/TiB$_2$ superlattices. After increasing the temperature from $T=400$ °C to $T=500$ °C a new satellite peak (-1) appeared on the left side of (001) common peak. At $T=600$ °C (-2) satellite peak for (002) main peak appears, and the previous satellite peaks becomes sharper and narrower compare to superlattices grown at higher or lower temperature than $T=600$ °C. After increasing the temperature to 700 °C and 800 °C the intensity of the main peaks and satellite peaks becomes lower and the peaks also become broader which is a sign of lower structural
quality compared to 600 °C. Therefore, the optimum temperature for growing CrB$_2$/TiB$_2$ superlattices is 600 °C.

Fig. 13. Superlattices with modulation period $\Lambda=4$ nm, thickness ratio $\Gamma=0.5$, and $N=50$ grown at different temperatures.

4.1.5 Effect of number of periods $N$

This part is a comparison between superlattices with different number of periods $N$, to see how the quality of the superlattices would change by increasing $N$. As can be seen from the X-ray diffraction pattern in Fig. 14 that for $\Lambda=4$ nm, until $N=50$, superlattice peaks become narrower with higher intensity which is the signature of a better quality superlattice. Then, by adding more layers during growth, the intensity of diffraction peaks is decreased and also new peaks are appeared which means that other lattice orientations are appeared and the structure is going to change from a perfect epitaxial superlattice to a semi-epitaxial structure. So, it is expected to see the superlattice structure with all planes oriented along {001} direction when having 50 periods or less.
Fig. 14. Superlattices with modulation period $\Lambda=4$ nm and thickness ratio $\Gamma=0.5$ grown at $T=600$ °C for three different number of periods $N$.

4.1.6 Various modulation periods

Another step to reach better quality CrB$_2$/TiB$_2$ superlattices is the comparison between different modulation periods $\Lambda$. A series of superlattices with modulation periods of 1 nm, 2 nm, 6 nm, 8 nm, and 10 nm are grown at constant pressure and temperature. The total thickness in all cases is 1 µm. So, number of periods $N$, is different for each film depends on its $\Lambda$. Fig. 15 demonstrates the X-ray diffraction pattern of films. At modulation period $\Lambda=1$ nm no superlattice reflections can be seen. After increasing the modulation period to $\Lambda=2$ nm two satellite peaks (-1 and +1) appear around (002) main peak. After increasing $\Lambda$ to 6 nm, higher order satellite peaks appear which can be a sign of a better structured film. In the superlattices with modulation period $\Lambda=8$ nm the main superlattice peaks at (001) and (002) becomes narrower and the intensity of the peak at (101) becomes lower which are the signs of having better crystalline quality superlattices. By increasing the modulation period to $\Lambda=10$ nm, the intensity of the main superlattice peaks at (001) and (002) decreases and the main peak at (101) becomes sharper. So, from this Fig. it can be concluded that the superlattices with modulation period $\Lambda=8$ nm have the best crystalline quality compared to other bilayer thicknesses. Another point from Fig. 15 is related to the intensity of the main peak (002) in $\Lambda=8$ nm and $\Lambda=10$ nm.
which becomes lower, and that is related to the multiplication of the structure factors of CrB$_2$ and TiB$_2$ and the bilayer thickness. For large modulation periods the intensity of the main peaks might become smaller depends on the position of peaks after convolution of structure factors.

![Graph showing X-ray diffraction patterns for different modulation periods.](image)

Fig. 15. Superlattices with different modulation period $\Lambda$ but the same total thickness of 1 $\mu$m. Other parameters such as growth temperature and Ar pressure are kept constant for all depositions.

4.2 Microscopy analyses

In this section the structure of CrB$_2$/TiB$_2$ superlattices using transmission electron microscopy will be discussed. Fig. 16 (a) shows an overview of the structure of the superlattices with modulation period $\Lambda=8$ nm using a Z-contrast STEM. Bright and dark layers are CrB$_2$ and TiB$_2$ respectively. The overview image illustrates that for about first 20 periods (which is also shown in the bright field TEM image in Fig. 16 (b)) there are flat interfaces between the layers and after that, grains started to grow at slightly different orientations, and overall quality of superlattices deteriorate with increasing roughness. High resolution (HRTEM) image in Fig. 16 (c) also shows the epitaxial growth of the superlattice along (001) direction close to the
substrate. Electron diffraction pattern in Fig. 16 (d) shows the superlattice reflection around (001) and (002) peaks. These are in agreement with XRD data on having a better quality superlattice structure for $\Lambda=8$ nm.

Fig. 16. Cross-sectional (a) Z-Contrast STEM overview (b) Bright field TEM (C) HRTEM, and (d) Electron Diffraction pattern (ED) corresponding to the sample with modulation period $\Lambda=8$ nm.

Fig. 17 which is related to the sample with modulation period $\Lambda=10$ nm shows that there is still a little misorientation of grains after about 20 periods (a). The slightly different orientation of grains in high magnification can be seen in Fig. 17(c). Comparing the electron diffraction of this sample (Fig. 17 (d)) and the sample with $\Lambda=8$ nm, tells that the quality of the latter with smaller period is higher. Both Fig. 16 and Fig. 17 illustrate the roughness increases by increasing the number of periods. In order to check if it would be possible to grow a better structure with epitaxial growth from the very first atomic layers starting from TiB$_2$ on the substrate, one sample with modulation period $\Lambda=8$ nm and TiB$_2$ as the first layer is grown.
Fig. 17. Cross-sectional (a) Z-contrast STEM overview (b) Bright field TEM (C) High Resolution TEM, and (d) Electron Diffraction pattern corresponding to the sample with modulation period $\Lambda=10$ nm.

Fig. 18 shows the Z-contrast STEM images of the samples with $\Lambda=8$ nm. The bright and dark layers corresponded to CrB$_2$ and TiB$_2$ respectively. The only difference between the two samples is the starting layer which is CrB$_2$ for (a) and TiB$_2$ for (b). The high magnification STEM image (inset in Fig. 18 (b)) shows the epitaxial growth of TiB$_2$ on Al$_2$O$_3$ (0001) substrate. However, no big difference between the structural quality of CrB$_2$/TiB$_2$ and TiB$_2$/CrB$_2$ superlattices is seen.
EDX maps in Fig. 19 show the elemental distribution of Cr and Ti in both samples with modulation period $\Lambda$=8 nm (a-c) CrB$_2$/TiB$_2$, (d-f) TiB$_2$/CrB$_2$. These maps illustrate that the thickness ratio $\Gamma$ is less than what was intended ($\Gamma$=0.43), and the thickness of TiB$_2$ layers is about one third of period $\Lambda$ ($\Gamma$=0.3). This means that CrB$_2$ layers are thicker and TiB$_2$ layers are thinner than expected, whereas, the modulation period is the same as expected value ($\Lambda$=8 nm). Line profiles extracted from EDX maps shows elemental distribution in the layers. In both cases in Fig. 20 (a) and (b), it seems that CrB$_2$ diffuses within the TiB$_2$ layers and Cr signal never goes to zero. Diffusion of CrB$_2$ into TiB$_2$ layers could be the reason of not being able to grow CrB$_2$/TiB$_2$ superlattices with very thin layers ($\Lambda$=1 nm). That is proved from the samples with modulation period $\Lambda$=1 nm which was discussed before and no superlattice reflections around its main Bragg peak could be seen.
Fig. 19. Energy Dispersive X-ray spectroscopy (EDX), (a-c) related to the sample with modulation period $\Lambda=8$ nm CrB$_2$/TiB$_2$, (d-f) sample with modulation period $\Lambda=8$ nm TiB$_2$/CrB$_2$.

Fig. 20. Line profile of EDX maps for samples with modulation period $\Lambda=8$ nm (a) CrB$_2$/TiB$_2$, (b) TiB$_2$/CrB$_2$. 
Fig. 21. illustrates cross-sectional TEM(a) and STEM(b) images related to sample with modulation period $\Lambda=1$ nm. The corresponding SAED pattern and HRTEM image are shown in the insets. From the SAED pattern in Fig. 21 (a) it can be calculated that the film has (002) fiber texture. Both bright field TEM and STEM images show the homogeneous structure of CrB$_2$ and TiB$_2$, and fine fibers can be seen in the high resolution STEM image in the inset of Fig. (b).

![Fig. 21. Cross-sectional (a) Bright field TEM, (b) Z-contrast STEM corresponding to the sample with modulation period $\Lambda=1$ nm, High resolution images, and Electron Diffraction pattern are shown in insets.](image_url)
EDX map and its line profile related to the sample with modulation period $\Lambda=1$ nm in Fig. 22 shows some variations of concentration of Cr and Ti in the line profile. Origin of this variation is not clearly understood.

Fig. 22. Line profile (a), and EDX maps (b-d) of the sample with modulation period $\Lambda=1$ nm.
4.3 Nanoindentation

Nanoindentation is a commonly used method for evaluation of the hardness of a thin film. In this method, the film is probed with a diamond tip, and the applied load and displacement or penetration depth \( h \) of the tip is recorded during the indentation. There are three different parts in one indentation; 1. The loading part. In this step, load is measured until it reaches the maximum applied load. 2. Hold part where the applied load is held for a time in order to monitor drift. 3. Unloading part where the load is declined gradually to zero. The final result is a load-displacement curve. Hardness and the recorded Young’s modulus \( E_r \) of the film can be obtained from the load-displacement curve by applying the method developed by Oliver and Pharr [29].

In nanoindentation, the hardness is calculated according to the following equation

\[
\text{Hardness} = \frac{P_{\text{max}}}{A}
\]

(5)

Where \( P_{\text{max}} \) is the maximum applied load, and \( A \) is the contact area of the tip. In the present work, the nanoindentation analyses for CrB\(_2\)/TiB\(_2\) superlattices grown on Al\(_2\)O\(_3\)(0001) are performed in an Ultra-Micro Indentation System with a sharp Berkovich diamond tip calibrated using a fused-silica standard sample. The load \( P \) is increased from 3 to 27 mN at increments of 0.5 mN, and the results are analyzed using the Oliver and Pharr method. Indents to depths \( \geq 10\% \) of the film thickness are excluded in the analysis. For doing hardness measurement 10 indents per sample are done and the average of the result for each sample is shown in Fig. 23.
As can be seen in Fig. 23, the hardness changes between 29 and 34 GPa for all samples. The lowest hardness value is related to the sample with modulation period of $\Lambda=1$ nm with about 29 GPa, and the highest hardness is related to the sample with $\Lambda=8$ nm with around 34 GPa. However, the error bars show that there is not a significant difference in hardness between the sample with modulation period $\Lambda=2$ nm, $\Lambda=6$ nm, and $\Lambda=8$ nm.
5. Conclusion

The main important conclusion in this study is that for the first time CrB$_2$/TiB$_2$ superlattices are grown by magnetron sputtering. Parameters optimization show that at $P_A=4$ mTorr, and the growth temperature of $T=600$ °C superlattices with modulation period of $\Lambda=8$ nm have the highest crystalline quality. Comparing CrB$_2$/TiB$_2$ and TiB$_2$/CrB$_2$ superlattices with the same modulation period $\Lambda=8$ nm show that there is not a big difference between the structural quality of these two superlattices. And finally, diffusion of CrB$_2$ into TiB$_2$ layers is observed.
6. References


