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ZrB₂ Thin Films

Growth and Characterization

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Cover: X-ray diffraction pole figures recorded from ZrB₂ thin films deposited on 4H-SiC(0001), Si(111), Al₂O₃(0001), and GaN(0001).

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Abstract

Zirconium diboride, ZrB_2 , is a ceramic material with bulk properties such as high melting point (3245 °C), high hardness (23 GPa), and low resistivity ($\sim 8 \mu\Omega\text{cm}$). Thin film growth of ZrB_2 using physical vapor deposition has suffered from problems with films deviating from stoichiometry and with high levels of contaminants, especially high oxygen content. The homogeneity range of ZrB_2 is very narrow, and consequently it is vital to achieve the correct stoichiometry to grow films with high crystalline order.

This thesis describes a direct current magnetron sputtering process to grow stoichiometric ZrB_2 thin films with a low degree of impurities. Growth of epitaxial ZrB_2 films was achieved on 4H-SiC(0001), Si(111) and Al_2O_3 (0001) substrates. The effect of deposition temperature and power applied on the sputtering target was investigated and showed that high power density (8.77 Wcm^{-2}) and high temperature (900 °C) resulted in films with the best composition and the highest crystal quality. ZrB_2 films on GaN(0001) templates exhibit an amorphous layer at the film-substrate interface and the resulting films are either polycrystalline or textured.

Resistivity measurements showed that the ZrB_2 thin films exhibit typical resistivity values of $\sim 100\text{-}250 \mu\Omega\text{cm}$ and that the resistivity decreased with increasing deposition temperature.

Nanoindentation was applied to assess the mechanical properties of the films. The epitaxial ZrB_2 films exhibit high elastic recovery and a hardness of $\sim 45\text{-}50 \text{ GPa}$, twice as high as the literature bulk value. In addition, evaluation of the mechanical properties was performed at high temperatures of up to 600 °C and showed that the epitaxial films retained a higher hardness, compared to textured ZrB_2 films and bulk, also at these temperatures.

Populärvetenskaplig sammanfattning

Kjell: Vad är det Lina jobbar med?

Linnea: Hon är tunnfilmsfysiker

Kjell: Va?! Är hon stumfilmsmusiker?

Ovan är ett samtal mellan min vän Linnea och hennes pappa Kjell. När jag fick det här samtalet återberättat för mig skrattade jag såklart men ändrade också mitt svar på frågan ”Vad jobbar du med?” från att säga att jag doktorerar i tunnfilmsfysik till att säga att jag forskar inom materialvetenskap. Samtalet fick mig helt enkelt att inse att få personer har någon relation till ordet tunnfilmsfysik. I den här sammanfattningen ska jag ändå försöka mig på att förklara vad just tunnfilmsfysik innebär.

En film är ett tunt skikt av ett material som lagts på ett annat material för att förbättra eller ändra det underliggande materialets egenskaper. Principen användes långt innan ordet tunnfilmsfysik kom till. Redan i det antika Egypten kunde man banka ut guld till oerhört tunna blad som sedan användes i dekorativt syfte. Tidigt började man också glasera keramik för att göra lerkrukor både vackra och ogenomträngliga för vatten. Mer nutida exempel är lackering av bilar för att förhindra rost och olika sorters beläggningar på glasögonglas för att t.ex. förhindra repor eller reflektioner.

Forskningsfältet tunnfilmsfysik handlar om att utveckla och förstå nya och redan existerande tunnfilmsmaterial. En tunn film kan vara allt från bara ett atomlager tjockt till ~1 mikrometer tjock. De flesta filmer som jag gjort är ungefär 400 nanometer tjocka. Som jämförelse kan nämnas att ett hårstrås radie är ungefär hundra gånger större än tjockleken på mina filmer.

En del av forskningen inom tunnfilmsfysik är riktad mot att lösa ett specifikt problem för en specifik tillämpning. Det kan t.ex. innebära utveckling av ett tunnfilmsmaterial för att förlänga livstiden för verktyg inom metallbearbetningsindustrin. Men en stor del av forskningen är även så kallad grundforskning där syftet med forskningen är att lära sig att förstå så mycket som möjligt om ett material för att i ett senare skede tillämpa den kunskapen för att lösa specifika problem. Min forskning är grundforskning och handlar om materialet zirkoniumdiborid (ZrB_2). ZrB_2 är en borid, alltså ett material baserat på grundämnet bor. Borider är tillsammans med karbider (baserade på

kol), nitrider (baserade på kväve) och oxider (baserade på syre) en del av en materialgrupp kallad keramer. En keram består av en metall, i mitt fall zirkonium, och en icke-metall, i mitt fall bor. Keramer har ofta hög smältpunkt, är kemiskt stabila, tål höga temperaturer, korroderar inte (löses inte upp i kontakt med omgivningen som järn som rostar eller koppar som ärgar), har hög hårdhet, är spröda och leder inte elektricitet. ZrB_2 har alla dessa egenskaper förutom att det till skillnad från de flesta keramer är elektriskt ledande. Den kombinationen av egenskaper gör ZrB_2 intressant att undersöka som tunnfilmsmaterial.

Egenskaperna hos ett material kan vara annorlunda när materialet är i form av en tunn film jämfört med en tjockare bit, så kallad bulk. Så det är inte säkert att tunna filmer av ZrB_2 leder elektricitet, även om ZrB_2 -bulk gör det eller att filmerna är lika hårda som bulk. En films egenskaper beror i hög grad på filmens mikrostruktur, alltså strukturen på en mikroskopisk skala. De flesta keramer är kristallina material, d.v.s. atomerna är ordnade i ett speciellt mönster, en kristallstruktur. Materialet kan bestå antingen av en enda stor kristall eller många små kristaller, så kallade korn. Kornen kan vara slumpmässigt ordnade i förhållande till varandra eller så kan alla korn vara riktade åt samma håll. Filmens egenskaper påverkas av hur välordnad den är. När kristallerna i en film riktar sig på ett visst sätt, baserat på hur det underliggande materialet (substratet) ser ut så kallas det epitaxi. Ett av målen med min forskning har varit att försöka växa epitaxiella filmer av ZrB_2 , vilket jag lyckats med.

För att framställa mina filmer har jag använt en metod som på svenska heter katodförångning men som kallas sputtring efter engelskans sputtering. Materialet som filmen ska byggas av är i form av en eller flera fasta källor, i mitt fall en ZrB_2 källa. Sedan tänds ett plasma (joniseras en ädelgas) och jonerna i plasmat träffar materialkällan (katoden) och skjuter (sputtrar) ut atomer ur källan. En del av atomerna hamnar på substratet och en film börjar växa. En förutsättning för att sputtring ska fungera är att det sker i en vakuumkammare där så mycket luft som möjligt har pumpats ut eftersom de atomer som ska bilda filmen måste ha möjlighet att komma fram till substratet utan att krocka eller reagera med andra atomer. I den kammare som jag använt mest är trycket ungefär en biljondel av normalt lufttryck.

Hur filmen kristalliserar beror på vilka processförhållanden som används under beläggningen, såsom temperatur, effekt lagd på källan och tryck. Dessa och andra parametrar påverkar även filmens sammansättning, alltså hur mycket av varje atomslag det finns i filmen. För ZrB_2 -filmer är

det viktigt att det finns dubbelt så mycket bor som zirkonium och att det finns så lite föroreningar (andra ämnen) som möjligt, i mitt fall främst syre och kol. Rätt sammansättning och en låg föroreningsgrad är viktigt eftersom det inte finns plats för extra atomer, av något slag, i kristallstrukturen. Finns det för många atomer av någon sort kan det orsaka att flera olika sorters kristallstrukturer bildas i filmen, något som kan förstöra filmens egenskaper. Att få till rätt sammansättning har tidigare varit ett problem vid sputtring av ZrB_2 -filmer men jag har lyckats belägga filmer med rätt förhållande mellan zirkonium och bor och med endast en liten del föroreningar.

Jag har också mätt egenskaper såsom hårdhet och elektrisk resistans och kan konstatera att mina filmer är både elektriskt ledande och mycket hårdare än ZrB_2 -bulk. Filmerna är hårda även vid höga temperaturer ($600\text{ }^\circ\text{C}$), vilket är lovande för potentiella tillämpningar.

Preface

This thesis is the result of my doctoral studies in the Thin Film Physics Division at the Department of Physics, Chemistry and Biology (IFM) at Linköping University between 2011 and 2016.

Parts of the results are published in scientific journals and the introductory chapters are based on my licentiate thesis *Growth and Characterization of ZrB_2 Thin Films*, Linköping Studies in Science and Technology. Licentiate Thesis No. 1614 (2013).

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During the course of research underlying this thesis, I was enrolled in *Agora Materiae*, a multidisciplinary doctoral program at Linköping University, Sweden.

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Included papers

Paper I **Direct current magnetron sputtered ZrB₂ thin films on 4H-SiC(0001) and Si(100)**

Lina Tengdelius, Mattias Samuelsson, Jens Jensen, Jun Lu, Lars Hultman, Urban Forsberg, Erik Janzén, and Hans Högberg
Thin Solid Films, 550, p. 285-290, 2014

Paper II **Magnetron sputtering of epitaxial ZrB₂ thin films on 4H-SiC(0001) and Si(111)**

Lina Tengdelius, Jens Birch, Jun Lu, Lars Hultman, Urban Forsberg, Erik Janzén, and Hans Högberg
physica status solidi (a), 211, p. 636-640, 2014

Paper III **Stoichiometric, epitaxial ZrB₂ thin films with low oxygen-content deposited by magnetron sputtering from a compound target: Effects of deposition temperature and sputtering power**

Lina Tengdelius, Grzegorz Greczynski, Mikhail Chubarov, Jun Lu, Urban Forsberg, Lars Hultman, Erik Janzén, and Hans Högberg
Journal of Crystal Growth, 430, p. 55-62, 2015

Paper IV **Hard and elastic epitaxial ZrB₂ thin films on Al₂O₃(0001) substrates deposited by magnetron sputtering from a ZrB₂ compound target**

Lina Tengdelius, Esteban Broitman, Jun Lu, Fredrik Eriksson, Jens Birch, Tomas Nyberg, Lars Hultman, and Hans Högberg
Acta Materialia, 111, p.166-172, 2016

Paper V **High-temperature nanoindentation of epitaxial ZrB₂ thin films**

Esteban Broitman, Lina Tengdelius, Ude D. Hangen, Jun Lu, Lars Hultman and Hans Högberg
Submitted for publication

Paper VI **ZrB₂ thin films deposited on GaN(0001) by magnetron sputtering from a compound source**

Lina Tengdelius, Jun Lu, Urban Forsberg, Xun Li, Lars Hultman, Erik Janzén, and Hans Högberg
Submitted for publication

Contributions to included papers

I took part in the planning of all included studies. I performed all the thin film growth. I conducted some of the X-ray diffraction $\theta/2\theta$ measurements, all of the pole figure measurements, except the ones in the supplementary material for **Paper III**, and took part in recording the reciprocal space maps. I measured the resistivity for **Paper I** and **Paper III**, but not **Paper IV**. The electron microscopy, composition analysis and nanoindentation were performed by co-authors. I took part in the evaluation of data and discussions of all results. I was responsible for writing **Papers I-IV** and **Paper VI** with input from the other co-authors. I helped edit the manuscript and made the figures for **Paper V**.

Not included papers

β -Ta and α -Cr thin films deposited by high power impulse magnetron sputtering and direct current magnetron sputtering in hydrogen containing plasmas

Hans Högberg, [Lina Tengdelius](#), Mattias Samuelsson, Jens Jensen, and Lars Hultman

Physica B: Condensed Matter, 439, p. 3-8, 2014

Reactive sputtering of δ -ZrH₂ thin films by high power impulse magnetron sputtering and direct current magnetron sputtering

Hans Högberg, [Lina Tengdelius](#), Mattias Samuelsson, Fredrik Eriksson, Esteban Broitman,

Jun Lu, Jens Jensen, and Lars Hultman

Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films, 32, p. 041510:1-8, 2014

List of tables and figures

Table 5.1 Typical levels of contaminants, measured by using ERDA, in ZrB ₂ thin films deposited on Si(100) substrates in an industrial scale HV deposition system.....	22
Table 5.2 Typical levels of contaminants, measured by using XPS, in ZrB ₂ thin films deposited on 4H-SiC(0001) substrates in a lab scale UHV deposition system with a sputtering power of 400 W at different deposition temperatures.	23
Table 5.3 Typical levels of contaminants, measured by using XPS, in ZrB ₂ thin films deposited in a lab scale UHV deposition system at a deposition temperature of 900 °C applying different sputtering powers.	23
Table 5.4 Epitaxial relationships for ZrB ₂ films deposited on 4H-SiC(0001), Si(111), and Al ₂ O ₃ (0001) substrates.	38
Table 5.5 Lattice parameters and film strain values calculated from RSMs recorded for ZrB ₂ films deposited on 4H-SiC(0001), Si(111), and Al ₂ O ₃ (0001) substrates.....	39
Fig. 2.1 Schematic illustration of a cross-section of a polycrystalline film showing that the grains are randomly oriented.....	3
Fig. 2.2 Schematic illustration of a cross-section of a fiber textured film and substrate showing that all grains are oriented the same way out-of-plane.....	4
Fig. 2.3 Schematic illustration of a film viewed from above showing that in a fiber textured film the grains are randomly oriented in-plane.....	4
Fig. 2.4 Schematic illustration of a film viewed from above showing that in a biaxial textured film all grains are oriented in the same way in-plane.....	5
Fig. 2.5 Schematic illustration of a substrate and film with perfect lattice match.....	6
Fig. 2.6 Schematic illustration of a substrate and film where the lattice parameter of the film is larger than that of the substrate causing compressive stress.	7
Fig. 2.7 Schematic illustration of a substrate and film where the lattice parameter of the film is smaller than that of the substrate causing tensile stress.	7
Fig. 2.8 Schematic illustration of a film and substrate where misfit dislocations have occurred due to high stresses in the film.	8
Fig. 2.9 Schematic illustration of a film and substrate that exhibit a 6:5 magic mismatch.	8

Fig. 3.1 Schematic illustration showing the layered structure of ZrB_2 . The Zr atoms are illustrated as large blue spheres and the B atoms as small yellow spheres.	11
Fig. 3.2 Schematic illustration showing the primitive unit cell of ZrB_2 and the crystallographic axes. The Zr atoms are illustrated as large blue spheres and the B atoms as small yellow spheres.	12
Fig. 3.3 Schematic illustration showing the ZrB_2 structure seen from the [0001] direction. The Zr atoms are illustrated as large blue spheres and the B atoms as small yellow spheres.	12
Fig. 3.4 Phase diagram for Zr-B. [5] Reprinted with permission of AMS International. All rights reserved.	14
Fig. 3.5 Phase diagram for Zr-C where γ is the ZrC phase. [5] Reprinted with permission of AMS International. All rights reserved.	14
Fig. 4.1 Schematic illustration of the magnetron setup for a) co-sputtering, b) reactive sputtering, and c) from a compound source.	16
Fig. 5.1 TEM image of a ZrB_2 thin film, with a dense and columnar structure, grown on an $\text{Al}_2\text{O}_3(0001)$ substrate. Adapted from [49] with permission of Elsevier.	25
Fig. 5.2 HRTEM image of a sharp interface between the ZrB_2 film and the $4\text{H-SiC}(0001)$ substrate. Adapted from [50] with permission of Wiley.	25
Fig. 5.3 HRTEM image of a ZrB_2 thin film grown on a $4\text{H-SiC}(0001)$ substrate. Adapted from [50] with permission of Wiley.	26
Fig. 5.4 Z-contrast image of a semi-coherent grain boundary in a ZrB_2 thin film grown on an $\text{Al}_2\text{O}_3(0001)$ substrate. Adapted from [49] with permission of Elsevier.	26
Fig. 5.5 TEM image exhibiting the rough surface structure of a ZrB_2 thin film grown on $4\text{H-SiC}(0001)$ using a sputtering power of 100 W. Adapted from [51] with permission of Elsevier.	27
Fig. 5.6 TEM image showing an amorphous/nanocrystalline layer at the film-substrate interface of a ZrB_2 thin film grown on a $4\text{H-SiC}(0001)$ substrate with no external heating.	28
Fig. 5.7 TEM image of a ZrB_2 thin film grown on a $\text{Si}(111)$ substrate where the substrate is exhibiting a wavy interface with amorphous material in the ‘valleys’.	29
Fig. 5.8 TEM image showing an amorphous/nanocrystalline layer at the film-substrate interface of a ZrB_2 thin film grown on a $\text{GaN}(0001)$ substrate.	30

Fig. 5.9 $\theta/2\theta$ diffractograms from ZrB_2 films grown on $4\text{H-SiC}(0001)$ substrates at different deposition temperatures in the range between room temperature and 900°C . The curves in gray are from films deposited in the industrial HV system and the curves in black are from films deposited in the UHV system. Adapted from [51,52] with permission of Elsevier.....	31
Fig. 5.10 Pole figures of ZrB_2 thin films deposited on $4\text{H-SiC}(0001)$ substrates at a) room temperature, b) 550°C , c) 600°C , d) 700°C , e) 820°C , and f) 900°C . All figures are of the $10\bar{1}1$ pole except c) which is of the 0001 pole. Adapted in part from [51] with permission of Elsevier.....	32
Fig. 5.11 $\theta/2\theta$ diffractograms from ZrB_2 films grown on $\text{Si}(111)$ substrates at different deposition temperatures in the range between 500°C and 900°C	33
Fig. 5.12 $\theta/2\theta$ diffractograms from ZrB_2 films grown on $\text{GaN}(0001)$ substrates at different deposition temperatures of 500°C and 900°C	34
Fig. 5.13 Pole figures of the $10\bar{1}1$ pole of ZrB_2 films grown on $\text{GaN}(0001)$ at a) 500°C and b) 900°C	35
Fig. 5.14 $\theta/2\theta$ diffractograms from ZrB_2 films grown on $4\text{H-SiC}(0001)$ substrates at different sputtering powers between 100 W and 400 W . Reprinted from [51] with permission of Elsevier.	35
Fig. 5.15 Pole figures of the $10\bar{1}1$ pole of ZrB_2 films grown on $4\text{H-SiC}(0001)$ with a sputtering power of a) 100 W , b) 200 W , c) 300 W , and d) 400 W . Reprinted from [51] with permission of Elsevier.....	36
Fig. 5.16 Pole figures showing a) the $10\bar{1}1$ pole of a ZrB_2 film deposited on a $4\text{H-SiC}(0001)$ substrate, and b) the $10\bar{1}1$ pole of the $4\text{H-SiC}(0001)$ substrate, c) the $10\bar{1}1$ pole of a ZrB_2 film deposited on a $\text{Si}(111)$ substrate, and d) the 220 pole of the $\text{Si}(111)$ substrate, e) the $10\bar{1}1$ pole of a ZrB_2 film deposited on a $\text{Al}_2\text{O}_3(0001)$ substrate, and f) the $10\bar{1}4$ pole of the $\text{Al}_2\text{O}_3(0001)$ substrate. Adapted from [49,50] with permission of Elsevier and Wiley.	37
Fig. 5.17 Resistivity values for ZrB_2 thin films grown on $4\text{H-SiC}(0001)$ substrates at different temperatures and sputtering powers. Reprinted from [51] with permission of Elsevier.....	40
Fig. 5.18 TEM image of a ZrB_2 film deposited on a $\text{Si}(100)$ substrate at room temperature showing the mark after nanoindentation. The top part of the image is a Pt layer deposited to protect the ZrB_2 film during TEM sample preparation.	41
Fig. 6.1 Schematic illustration of Bragg's law.	43

Fig. 6.2 Notation of the angles in XRD.	44
Fig. 6.3 $\theta/2\theta$ diffractogram with a linear intensity scale from a ZrB_2 film grown on an $\text{Al}_2\text{O}_3(0001)$ substrate.	45
Fig. 6.4 $\theta/2\theta$ diffractogram with a logarithmic intensity scale from a ZrB_2 film grown on an $\text{Al}_2\text{O}_3(0001)$ substrate.	45
Fig. 6.5 Pole figures of the $10\bar{1}1$ pole of a ZrB_2 film grown on a) $\text{GaN}(0001)$ at 500°C , b) $\text{GaN}(0001)$ at 900°C , and c) $4\text{H-SiC}(0001)$ at 900°C	46
Fig. 6.6 Schematic illustration of how a RSM is recorded by consecutive coupled 2θ - ω scans. ..	47
Fig. 6.7 RSMs for a film grown on $\text{Si}(111)$ showing a) the ZrB_2 0002 lattice point, and b) the ZrB_2 $10\bar{1}3$ lattice point. In the lower left corner the 313 lattice point from the substrate is seen. Adapted from [50] with permission of Wiley.	48
Fig. 6.8 Schematic illustration of the set-up for a four-point probe.....	51
Fig. 6.9 Schematic illustration of the energy levels interesting for XPS analysis.	53
Fig. 6.10 High resolution XPS spectra of the Zr 3d and B 1s photoelectron region from a ZrB_2 film deposited at 900°C and with 400 W applied to the target. The dotted line represents the as deposited film and the solid line is after 180 s of sputter cleaning. Reprinted from [51] with permission of Elsevier.	54
Fig. 6.11 Z-contrast image with superimposed EDX maps showing Zr (red) and Ga (green).	55
Fig. 6.12 Load-displacement curve recorded from a ZrB_2 film deposited on $\text{Al}_2\text{O}_3(0001)$	56

Abbreviations

A	contact area
CTEM	conventional transmission electron microscopy
CVD	chemical vapor deposition
DCMS	direct current magnetron sputtering
E_B	binding energy
EDX	energy-dispersive x-ray spectroscopy
EELS	electron energy loss spectroscopy
E_{kin}	kinetic energy
EM	electron microscopy/electron microscope
E_r	reduced Young's modulus
ERDA	elastic recoil detection analysis
h	displacement/penetration depth
HRTEM	high resolution transmission electron microscopy
HV	high vacuum
h ν	photon energy
L	applied load
LOM	light optical microscope
PVD	physical vapor deposition
RSM	reciprocal space map
SAED	selected area electron diffraction
SEM	scanning electron microscopy/scanning electron microscope
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy/ transmission electron microscope
ToF-ERDA	time-of-flight elastic recoil detection analysis
UHV	ultra-high vacuum
W_e	elastic recovery
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction
ϕ	work function

Contents

Abstract	I
Populärvetenskaplig sammanfattning	III
Preface	VII
Acknowledgments	IX
Included papers	XI
Not included papers	XIII
List of tables and figures	XV
Abbreviations	XIX
1 Introduction	1
1.1 Aim	2
1.2 Outline	2
2 Texture and epitaxy	3
2.1 Texture	3
2.2 Epitaxy	5
2.2.1 Conditions for epitaxial growth	6
3 Zirconium diboride	11
3.1 Crystal structure	11
3.2 Properties	13
3.3 Phase diagram	13
4 Methods for thin film synthesis	15
4.1 Chemical vapor deposition	15
4.2 Magnetron sputtering	16
5 Results and discussion	19
5.1 Film stoichiometry	19
5.2 Film contaminants	21
5.3 Microstructure	24
5.4 Film structure	30
5.4.1 Influence of deposition temperature	31
5.4.2 Influence of sputtering power	35

5.4.3	Epitaxial relationships	36
5.4.4	Film strain	38
5.5	Film properties	39
5.5.1	Resistivity	39
5.5.2	Mechanical properties	40
6	Characterization methods	43
6.1	X-ray diffraction	43
6.1.1	$\theta/2\theta$	44
6.1.2	Pole figures	46
6.1.3	Reciprocal space maps	47
6.2	Electron microscopy	48
6.2.1	Scanning electron microscopy	49
6.2.2	Transmission electron microscopy	49
6.3	Resistivity measurements	51
6.4	Composition analysis	52
6.4.1	Elastic recoil detection analysis	52
6.4.2	X-ray photoelectron spectroscopy	52
6.4.3	Energy-dispersive X-ray spectroscopy	54
6.4.4	Electron energy loss spectroscopy	55
6.5	Nanoindentation	56
7	Conclusions	59
8	Future outlook	61
	References	63
	Papers	

1 Introduction

Today thin films are present in one way or another in most people's lives. They can be in the form of anti-reflective coatings on glasses, nonstick coatings in frying pans, as protective coatings in food packages or in the microelectronics in cellphones, tablets and other electronic devices. Coating a material with a thin film can greatly alter or enhance the properties of the underlying material in order to make it more suitable for a given application. New technologies and products are developed every day and with them come demands for new materials with specific properties.

In the development and tailoring of new thin film materials it is vital to get a thorough understanding of how the films grow and how changing a deposition parameter will affect the film properties. Fundamental research in thin film physics is focused on enhancing the understanding of thin film growth, developing new materials and increasing the knowledge of materials with potential to be useful in practical applications.

Transition metal borides are compounds consisting of a transition metal and boron. They are ceramic materials with properties such as high hardness, high wear resistance, high melting points, chemical inertness, and often metallic conduction [1]. These properties make transition metal borides promising for several potential applications, for example as electrical contact materials in demanding environments, in aerospace applications and as hard protective coatings in metal cutting [2]. The most common crystal structure for the transition metal borides is the AlB_2 -type. This structure is often formed by the transition metal borides from group 4-6 in the periodic table [1]. Within the AlB_2 -type transition metal diborides, the group 4 diborides, i.e. TiB_2 , ZrB_2 , and HfB_2 are the most stable [3,4]. The phase diagrams for these compounds [5] reveal that Ti-B is a more complex system than Zr-B and Hf-B with multiple competing phases, whereas in the Zr-B material system there are only two phases, ZrB_2 and ZrB_{12} . ZrB_2 and HfB_2 are very similar but the larger

mass difference between Hf and B, compared with between Zr and B, adds complexity to the sputtering process so for this thesis ZrB_2 was chosen as the material of study.

1.1 Aim

The aim of the research project on which this thesis is based was to enhance the knowledge of ZrB_2 as thin films and to develop a magnetron sputtering process that resulted in high quality thin films. High quality in this case means stoichiometric films with a low degree of impurities and high crystalline ordering. Another goal has been to achieve epitaxial growth of ZrB_2 thin films using direct current magnetron sputtering (DCMS) from a compound source.

1.2 Outline

This thesis describes the growth and characterization of ZrB_2 thin films. After this general introduction, the thesis will continue with a chapter on texture and epitaxy. A chapter on the structure and properties of ZrB_2 will follow. Chapter four describes vapor based methods to grow thin films. The fifth chapter highlights results from my own research and attempts to explain how the results in the included papers relate to each other. Chapter six describes the methods applied to characterize the ZrB_2 films. Conclusions and an outlook towards future research in this area concludes the introductory part of this thesis. At the very end the included papers can be found.

2 Texture and epitaxy

2.1 Texture

Texture is the distribution of crystallographic orientations in a polycrystalline sample. If the orientations of the grains are completely random, see Fig. 2.1, the sample has no texture and is said to be polycrystalline. This was the case for the films grown on Si(100) and 4H-SiC (0001) at 550 °C in **Paper I** and films grown on GaN(0001) with a reduced preheating time or at a deposition temperature lower than 900 °C in **Paper VI**.

Fig. 2.1 Schematic illustration of a cross-section of a polycrystalline film showing that the grains are randomly oriented.

If there is a preferred orientation, the sample is textured and the degree of texture is determined by the fraction of grains having the preferred orientation. A sample can be weakly, moderately, or strongly textured. In so called fiber textured samples a certain plane in the deposited crystal is preferentially parallel to the plane of the substrate surface so that by looking at a cross-section of the film it can be seen that all the grains are aligned in the same way out-of-plane, see Fig. 2.2.

Fig. 2.2 Schematic illustration of a cross-section of a fiber textured film and substrate showing that all grains are oriented the same way out-of-plane.

However, looking at the film from the top will show that the film is randomly oriented with regards to the in-plane orientation, see Fig. 2.3. The films grown without external heating in **Paper I**, on

Fig. 2.3 Schematic illustration of a film viewed from above showing that in a fiber textured film the grains are randomly oriented in-plane.

both Si(100) and 4H-SiC(0001) substrates, showed a fiber textured structure, as did some of the films grown on GaN(0001) in **Paper VI**.

On the other hand, if the film has a specific orientation in-plane, see Fig. 2.4, the sample is said to have biaxial texture which was the case for the films grown at 900 °C on Si(111) in **Paper II**, on 4H-SiC(0001) in **Paper II**, **Paper III**, and **Paper V** as well as for films deposited on Al₂O₃(0001) in **Paper IV**.

Fig. 2.4 Schematic illustration of a film viewed from above showing that in a biaxial textured film all grains are oriented in the same way in-plane.

2.2 Epitaxy

The word epitaxy has its origin in the greek words *epi* meaning ‘above’ and *taxis* meaning ‘in ordered manner’. In materials science, the term refers to the deposition of a layer onto a crystalline substrate where the crystalline orientation of the substrate imposes an order on the orientation of the film. Sometimes the word epitaxy is used to describe all films where there is any relation

between film and substrate and sometimes it is used only for single crystal films. In this thesis, the word epitaxial will describe a film that exhibits biaxial texture and where the crystallographic axis of the deposited layer is aligned to the axis of the substrate. Growth of such films was achieved in **Paper II-V**.

If the film and substrate consist of the same material it is called homoepitaxial growth, whereas if the film is of another material than the substrate it is termed heteroepitaxial growth. Homoepitaxial growth is usually used in order to grow films with higher crystal quality, less impurities and/or different doping characteristics than the underlying substrate. Heteroepitaxy is used in order to alter the properties of a given material or when this kind of growth is the only alternative in order to achieve a crystal of high quality of the desired material. In this thesis only heteroepitaxial growth is addressed.

2.2.1 Conditions for epitaxial growth

When attempting heteroepitaxial growth, one important factor is that the lattice parameters of the film and substrate should not differ too much, otherwise defects will occur due to stresses in the film. The misfit parameter, f , can be calculated from the lattice constants, a , according to

$$f = \frac{a(\text{substrate}) - a(\text{film})}{a(\text{substrate})}$$

If $f = 0$, i.e. the lattice constant of the film is the same as the lattice constant of the substrate, there will be no stresses due to a lattice mismatch, see Fig. 2.5. This is the case for homoepitaxial growth.

Fig. 2.5 Schematic illustration of a substrate and film with perfect lattice match.

If $f < 0$, i.e. the lattice constant of the film is larger than the lattice constant of the substrate, the film will experience compressive stress in order to match the substrate, see Fig. 2.6.

Fig. 2.6 Schematic illustration of a substrate and film where the lattice parameter of the film is larger than that of the substrate causing compressive stress.

If $f > 0$, i.e. the lattice constant of the film is smaller than the lattice constant of the substrate, the film will experience tensile stress in order to match the substrate, see Fig. 2.7.

Fig. 2.7 Schematic illustration of a substrate and film where the lattice parameter of the film is smaller than that of the substrate causing tensile stress.

If the mismatch between film and substrate lattices is too large the film will relax, which will result in the occurrence of misfit dislocations, see Fig. 2.8. Heteroepitaxial growth is possible when $f \leq 9\%$.

Fig. 2.8 Schematic illustration of a film and substrate where misfit dislocations have occurred due to high stresses in the film.

Nonetheless, for some substrate/film systems, heteroepitaxial growth has been shown to be possible despite a large mismatch between film and substrate lattice parameters. This occurs when the length of a number of unit cells in the film correspond well to the length of another number of unit cells in the substrate, see Fig. 2.9.

Fig. 2.9 Schematic illustration of a film and substrate that exhibit a 6:5 magic mismatch.

Two such examples have been employed in this thesis. First ZrB_2 on $\text{Si}(111)$, where the misfit is as large as 17.5 %, but epitaxial growth is still possible due to a so called 6:5 coincidence or ‘magic mismatch’ where the size of 6 unit cells in the film matches the size of 5 unit cells in the substrate [6], so that the misfit becomes just 0.9 %. The second example is ZrB_2 on Al_2O_3 . In this case there are two ways of realizing the magic mismatch, first a 3:2 coincidence where the mismatch is 0.11 % between the Zr lattice in the film and the Al lattice in the substrate, and second a 7:8 coincidence with a mismatch of 0.84 % between the Zr lattice in the film and the O lattice in the substrate [7].

When attempting heteroepitaxial growth thermal expansion coefficients of the film and substrate materials need to be considered, since these determine the temperature dependence of the materials' lattice constants. The coefficients for the two materials need to be quite similar so the effect of the temperature on the film and substrate is more or less the same and does not cause the lattice parameter of either the film or substrate to expand considerably more than the other when heated. In **Paper VI** heteroepitaxial growth of ZrB_2 on GaN was attempted and the choice of substrate was partly due to the close match of thermal expansion coefficients for these materials, with values of $5.9 \cdot 10^{-6} \text{ K}^{-1}$ [8] and $5.6 \cdot 10^{-6} \text{ K}^{-1}$ [9] for ZrB_2 and GaN, respectively.

In order for a film to grow epitaxially, the atoms of the deposited material need to be able to find their equilibrium positions. Consequently, the adatoms need sufficient mobility so they do not get 'trapped' at a non-optimal position. This is usually achieved by applying a high deposition temperature.

For all epitaxial growth, heteroepitaxial as well as homoepitaxial, a high-quality substrate without surface contamination in the form of e.g. native oxide or adventitious carbon is important in order to allow the film to nucleate properly.

3 Zirconium diboride

3.1 Crystal structure

ZrB₂ is a hexagonal material with an AlB₂-type structure and its space group is number 191 [10]. The B atoms form honeycombed, graphite-like sheets that are stacked between hexagonal close packed Zr layers, see Fig. 3.1. The unit cell contains $8 * \frac{1}{8} = 1$ Zr atom positioned in the corners of the unit cell and two B atoms in the interstitial positions at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$, see Fig. 3.2. The cell parameters of ZrB₂ is 3.17 Å in the *a* direction and 3.53 Å in the *c* direction [10]. In Fig. 3.3 the 0001-plane of ZrB₂ can be seen.

Fig. 3.1 Schematic illustration showing the layered structure of ZrB₂. The Zr atoms are illustrated as large blue spheres and the B atoms as small yellow spheres.

Fig. 3.2 Schematic illustration showing the primitive unit cell of ZrB₂ and the crystallographic axes. The Zr atoms are illustrated as large blue spheres and the B atoms as small yellow spheres.

Fig. 3.3 Schematic illustration showing the ZrB₂ structure seen from the [0001] direction. The Zr atoms are illustrated as large blue spheres and the B atoms as small yellow spheres.

3.2 Properties

ZrB₂ exhibit ceramic properties such as high hardness (23 GPa) and high melting point (3245 °C) originating from the covalent type of bonding between the Zr and B atoms as well as between the B atoms in the honeycombed sheet [8]. ZrB₂ is also wear and corrosive resistant [11]. In addition, ZrB₂ has a bulk resistivity of ~8 μΩcm [12], which is even lower than its parent metal Zr with a resistivity of ~40 μΩcm [13]. The electrical conductivity of ZrB₂ stems from metal-metal bonding and electron transfer from the metal to the B sheet.

A small lattice mismatch between film and substrate is, as explained in Section 2.2.1, essential to grow epitaxial films. The lattice parameter of 3.17 Å in the *a* direction gives ZrB₂ a small lattice mismatch to technologically important semiconductor-materials such as silicon carbide, 4H-SiC(0001), and gallium nitride, GaN(0001), with values of -3.8 % [14] and 0.6 % [15] respectively, as well as magic mismatches to Si(111) and Al₂O₃(0001) (see Section 2.2.1).

3.3 Phase diagram

From the phase diagram of Zr-B in Fig. 3.4 it can be seen that ZrB₂ is a line phase, i.e. it has a narrow homogeneity range of less than 1 %, meaning that the B to Zr ratio cannot deviate much from the optimal value of 2. Any excess Zr or B atoms will not be accommodated in the structure but instead result in unwanted phase separation, thus disrupting the sought epitaxial growth conditions.

ZrB₂ is also sensitive to contaminants, such as oxygen, since the presence of a foreign element during nucleation of ZrB₂ will likely cause undesired chemical reactions and possibly hamper the epitaxial growth.

These properties, shown by ZrB₂, are in contrast to, e.g. the transition metal carbides and nitrides that are characterized by large homogeneity ranges [16] as well as possible solid solution of oxygen [17], making sputtering of carbides and nitrides more forgiving than borides. The phase diagram for Zr-C can be seen in Fig. 3.5 where the ZrC phase is marked as γ.

Fig. 3.4 Phase diagram for Zr-B. [5] Reprinted with permission of AMS International. All rights reserved.

Fig. 3.5 Phase diagram for Zr-C where γ is the ZrC phase. [5] Reprinted with permission of AMS International. All rights reserved.

4 Methods for thin film synthesis

Vapor-based thin film synthesis techniques are divided into two groups; chemical vapor deposition (CVD) and physical vapor deposition (PVD). PVD includes several methods such as evaporative deposition, pulsed laser deposition, cathodic arc deposition, and sputtering.

ZrB₂ thin films have been grown by CVD [6,7,11,18-24], pulsed laser deposition [25,26], e-beam deposition [26-28], sputtering of reactive multilayers [29], and sputtering from a compound source [30-43].

In this thesis only magnetron sputtering was used. Although CVD is not used to grow the ZrB₂ films in this thesis, it is still of importance since the method in **Papers II-VI** is inspired, in part, by previously developed CVD processes. In addition, the GaN template applied as a substrate in **Paper VI** was grown by CVD. Therefore brief descriptions of both CVD and magnetron sputtering are included in the following sections.

4.1 Chemical vapor deposition

CVD is a deposition method based on the decomposition and chemical reactions of reactive gaseous species on the substrate surface. The chemical reactions in CVD often require a high substrate temperature. The starting materials in CVD are called precursors. Either one single precursor, containing all the elements of the desired film, is used or the different elements are provided from several precursors. It is important that any additional atoms in the precursors, which are not of interest for growing the film, can form volatile species in order to not get incorporated in the film. To deposit ZrB₂ thin films the most common route has been to use the single precursor Zr(BH₄)₄ [6,7,18,20,21,23]. These processes are characterized by a typical deposition temperature of 900 °C and low deposition rates (0.3-1.4 nm/min). The fact that all epitaxial ZrB₂ films grown by CVD have more or less exclusively been grown at 900 °C was an important reason for applying

a deposition temperature of 900 °C when attempting epitaxial growth in **Paper II**. The GaN template, applied as a substrate in **Paper VI**, was grown by metal organic chemical vapor deposition from $\text{Ga}(\text{CH}_3)_3$ and NH_3 at 1050 °C [44].

4.2 Magnetron sputtering

Sputtering is a technique where an inert gas is used to eject (sputter) atoms from a target (source material). The inert gas, usually Ar, is ionized by collision with other Ar atoms or with secondary electrons. A negative bias is applied to the target to accelerate the Ar^+ ions towards it and cause target atoms to be sputtered. The sputtered species are then transported to the substrate surface where they condense and form a film. For sputtering to occur, a relatively high Ar pressure must be used but this is unfavorable since the sputtered target atoms are scattered by the Ar species on their way towards the substrate, which reduces the growth rate. To reduce this problem, the degree of ionization close to the target surface can be enhanced by placing magnets underneath the target to trap electrons in an magnetic field, which is the principle of magnetron sputtering. More Ar^+ ions gives a higher sputtering rate which in turn gives a higher growth rate.

Growing a binary compound such as ZrB_2 can be done in three ways:

- By using two targets (co-sputtering), see Fig. 4.1 a).
- By using one target and one reactive gas (reactive sputtering), see Fig. 4.1 b).
- By using one target containing both the desired atoms (compound sputtering), see Fig. 4.1 c).

Fig. 4.1 Schematic illustration of the magnetron setup for a) co-sputtering, b) reactive sputtering, and c) from a compound source.

To use co-sputtering to grow ZrB_2 films, a B-target would have to be used. However, B is insulating and a conductive target is required when using DCMS, which is the sputtering method applied in this thesis, to avoid charge build-up on the target surface. Insulating targets can be sputtered using radiofrequency sputtering, where the sign of the bias applied on the target is varied at a high rate but this requires other, more expensive power supplies and results in lower sputtering rates. Therefore, co-sputtering was ruled out as an alternative for this thesis.

Reactive sputtering offers the opportunity to control the relative amount of each constituent in the film, since the pressure of the reactive gas can be regulated. However, reactive sputtering requires a suitable reactive gas to be available. In the case of ZrB_2 there is no evident gas that can serve as the B source. The most natural candidate diborane, B_2H_6 , is unfortunately both explosive and highly toxic, making it impossible to work with in our available deposition systems. Furthermore, B_2H_6 has been shown to cause substantial target poisoning when depositing the related material TiB_2 [45].

The third alternative for sputtering ZrB_2 is to use a compound source and this alternative was chosen for this thesis. A disadvantage of using a compound target is that the composition of the resulting film is not always the same as the composition of the target, due to different energies and angular distribution of the different species. Before reaching a steady state the film will be enriched with the element with the highest sputtering yield. In addition, deviations from stoichiometry can occur due to different sticking probabilities for the elements, and composition can also be affected by e.g. growth temperature, substrate bias and substrate material. Furthermore, atoms at the film surface can be resputtered, and lighter elements are resputtered more easily compared to heavier elements.

The magnetron sputtering technique used in this thesis is DCMS where a constant power is applied to the target. DCMS results in a low degree of ionization of the sputtered material (less than 10 % for metals) which means that the majority of the sputtered flux is neutral. To increase ionization, and thereby the deposition rate, higher power densities need to be applied to the target. However, this can only be done to a certain point, or the target will be overheated. [46]

5 Results and discussion

In this chapter I have attempted to relate the most important findings in each paper to each other. For in-depth discussions of each result and comparison to the literature, the reader is referred to the individual papers at the end of the thesis.

A number of methods have been applied to characterize my films. If the reader is unfamiliar with any of these methods and finds that he or she would like some more background it is recommended to read the appropriate section in Chapter 6.

5.1 Film stoichiometry

As mentioned in Section 3.3, the ZrB_2 crystal structure can only accommodate a small number of extra atoms of either Zr or B. Large deviations of the B/Zr ratio from the optimal value of 2 will cause phase separation. Consequently, growing films with high crystal quality requires a process enabling the growth of stoichiometric films.

Studies on sputtered ZrB_2 films have reported both substoichiometric [31,32] and overstoichiometric films [35,39]. Thus, the first goal of this research project was to achieve growth of stoichiometric films and investigate which deposition parameters affect the stoichiometry and how.

For **Paper I** an industrial high vacuum (HV) deposition system was chosen to grow the films based on user friendliness of the system, opportunity to directly transfer the developed process to industry conditions and successful pre-studies using this deposition system. The film composition was evaluated using time-of-flight elastic recoil detection analysis (ToF-ERDA) which showed that most films had a B/Zr ratio of 1.97-2.00. Thus, the first goal of sputtering stoichiometric ZrB_2 films

had been achieved. However, I also wanted to know how robust the deposition process was and which deposition parameters that were important for the stoichiometry.

Parameters investigated were temperature (no external heating, 400 °C, and 550 °C), speed of the turbomolecular pumps (66 %, 100 %) and substrate bias (-20 V, -40 V, -60 V, and -80 V).

The reason for testing different speeds of the turbomolecular pumps was to determine if the residual gas had a large impact on the composition of the films. The results showed no significant difference in the B/Zr ratio between films deposited with either 66 % or 100 % speed of the turbomolecular pumps, under otherwise the same deposition conditions.

The temperature in the investigated temperature range did not affect the stoichiometry in itself, but the combination of 550 °C and a substrate bias of -80 V yielded substoichiometric films with a B/Zr ratio of 1.84-1.88. When applying a substrate bias voltage, the energy and flux of the incident particles are modified due to an alteration of the electric fields near the substrate. Several of the properties of the film may be affected by a bias voltage, including film morphology, density, grain size, preferred orientation, adhesion to the substrate, residual stresses in the film, and composition [47]. When the film surface is bombarded by energetic particles, the surface mobility of adatoms is elevated. Consequently, applying a substrate bias voltage is a way to achieve sufficient adatom mobility for epitaxial growth. However, it has been suggested that a high bias causes resputtering of B when depositing ZrB₂ films from a compound target [39]. Although a substrate bias of -80 V is much lower than the bias voltage of -400 V in that study, it is possible that the preferential resputtering of B is facilitated at elevated temperatures.

During the experiments which became the foundation for **Paper II** and **Paper III**, I believed I had a substrate bias of -80 V, but later found out that the substrate bias in the deposition system was not working properly. It is unclear if the substrate bias was working at the time of my depositions, but as I have later conducted experiments without applying a substrate bias with the same results, it is likely that the substrate bias was not working and that all films were deposited at floating potential. Based on all of the above results it can be concluded that growth of stoichiometric films is best performed without applying a substrate bias or at least with a bias below -80 V.

In **Paper III** the effect of sputtering power applied to the target, in the range between 100 and 400 W, and the deposition temperature, in the range between 500 °C and 900 °C, were investigated.

In that study the method used for compositional analysis was X-ray photoelectron spectroscopy (XPS). The change of technique from ToF-ERDA to XPS was mainly due to availability since at this time an XPS system had been purchased to my division, whereas for ERDA the analysis had to be performed at Uppsala University. The B/Zr ratios obtained by XPS were in good agreement with the results from ERDA for the same samples.

The XPS analysis showed that all temperatures yielded near-stoichiometric films with a B/Zr ratio between 2.06 and 2.12. The results indicate a slightly B-rich composition, but it should be noted that these values are within the typical confidence interval for XPS of $\pm 5\%$ and that the quantitative analysis is somewhat complicated by the closeness of the Zr 3d_{3/2} and B 1s peaks in the XPS spectrum, especially for samples containing much oxygen.

Sputtering power values of 300 W and 400 W yielded near-stoichiometric films whereas values of 100 W and 200 W resulted in films with a B/Zr ratio of around 1.5. The quantitative analysis in this case is further complicated by the high oxygen levels in these films (see Section 5.2), causing the Zr 3d_{3/2} peak from zirconium oxide to almost overlap with the B 1s peak.

To summarize, the deposition temperature and the residual gas (speed of turbomolecular pumps) does not substantially influence the stoichiometry of ZrB₂ films, whereas high bias voltages, in combination with elevated temperatures, as well as low sputtering powers result in offstoichiometric films.

5.2 Film contaminants

A high degree of film contaminants will cause the film properties to degrade, e.g. oxygen have been shown to have a negative impact on the electronic properties of ZrB₂ films [31,48]. The literature shows that ZrB₂ films, sputtered from a compound target, often exhibit a high level of contaminants, especially oxygen [31,32,40,43,48]. In Table 5.1 typical contaminant levels, measured by ERDA, can be seen for the films grown in the industrial HV deposition system in the study that was the basis for **Paper I**.

Table 5.1 Typical levels of contaminants, measured by using ERDA, in ZrB₂ thin films deposited on Si(100) substrates in an industrial scale HV deposition system.

Contaminant	≤ [at%]
Ar	0.2
C	0.4
H	0.1
N	0.1
O	1

For this study, no clear trends in the level of impurities could be seen based on speed of the turbomolecular pumps, deposition temperature, or applied substrate bias for the bulk of the film. However, there is more oxygen at the interface between the Si(100) substrate and the film, in the films grown with no external heating compared to those grown at elevated temperatures. This can partly, but not completely, be attributed to the thin native oxide on the Si(100) substrates. So for **Paper II** and **Paper III** both the Si and SiC substrates were cleaned thoroughly including an etching step with HF to remove the native oxide. It is likely that some of the oxygen stems from oxygen containing species adsorbed on the surface when no heating is applied. In a HV system the residual gas consists mainly of water vapor so it is convenient to think that this is the largest contribution for the oxygen. On the other hand, if that was the case, we would probably see more hydrogen in the films as well. Furthermore, the fact that the speed of the turbomolecular pumps made no difference indicate that the impact of the residual gas is low. Therefore, we suggest that the oxygen originates, at least in part from the target material and that the reason that we see less oxygen in the bulk of the film, compared to at the film-substrate interface, is that the substrate is gradually heated by the energetic flux of deposited material during deposition, which increases the probability of desorption of unreacted oxygen.

For **Paper II** and all of the following papers, the deposition system was changed to a lab scale ultra-high vacuum (UHV) system. This was done mainly due to the fact that the maximum possible deposition temperature in the industrial HV system is 550 °C and in the lab scale system 900 °C. Changing from a HV system to an UHV system also decreases the residual gas and hence its potential impact on the level of contaminants further.

In **Paper III**, where composition analysis was performed using XPS, there is a trend of increased oxygen content in films deposited at lower temperatures and at lower sputtering power, see Table 5.2 and Table 5.3. We do not think that the large amount of oxygen, in films deposited at 100 W and 200 W, originate mainly from the film itself. Instead, we believe that the source of the oxygen is oxygen containing species that dissolve in voids in the films, when the films are subjected to the atmosphere after deposition. For results on the microstructure of these films, see Section 5.3.

Table 5.2 Typical levels of contaminants, measured by using XPS, in ZrB₂ thin films deposited on 4H-SiC(0001) substrates in a lab scale UHV deposition system with a sputtering power of 400 W at different deposition temperatures.

Temp [°C]	O [at%]	C [at%]
900	2.99	2.20
820	2.82	1.59
700	3.53	1.42
600	3.56	1.03
500	4.17	1.21

Table 5.3 Typical levels of contaminants, measured by using XPS, in ZrB₂ thin films deposited in a lab scale UHV deposition system at a deposition temperature of 900 °C applying different sputtering powers.

Power [W]	O [at%]	C [at%]
400	2.99	2.20
300	3.30	1.42
200	18.90	3.82
100	26.46	7.88

The levels of both oxygen and carbon are higher in the films deposited in the study for **Paper III** than in those deposited for **Paper I** for all deposition conditions. However, we believe that this discrepancy is mostly due to the difference in characterization techniques which is supported by measurements of the same sample with both techniques where ERDA gives oxygen concentrations of ~1 at% and XPS ~5-6 at%. ERDA is a bulk technique where the result is an average of the

amount of impurities in the entire film, whereas XPS is a surface sensitive technique analyzing only the first few nm of the sample surface. To avoid measuring only the contaminants on the sample surface, the results in Table 5.2 and Table 5.3 are after 180 s of sputter cleaning. Hydrogen cannot be measured with XPS, and nitrogen and argon was below the detection limit of this technique. Furthermore, since we believe that at least part of the oxygen stems from the compound target, differences in oxygen content can be due to variations in the quality of the different targets used in **Paper I** and **Paper III**. The hypothesis of the target being a source of oxygen is supported by XPS analysis of a target piece exhibiting ~19 at% oxygen, even after 25 min of sputter-cleaning.

To summarize, the level of contaminants in my films is low compared to other sputtered films. We can see a trend of decreased amounts of oxygen when increasing the temperature from 500 °C to 900 °C, and sputtering with low power density on the target yields films with a high degree of both oxygen and carbon. We believe that at least some of these contaminants originate from the target material which makes our process dependent on the availability of high quality targets.

5.3 Microstructure

In this thesis growth of ZrB_2 thin films on the substrates Si(100), Si(111), 4H-SiC(0001), Al_2O_3 (0001) and GaN(0001) have been studied. The microstructure of these films have been studied using electron microscopy (EM), mainly transmission electron microscopy (TEM). The majority of the films have been found to have a dense, columnar microstructure with a smooth surface. An example of such a film microstructure is seen in Fig. 5.1.

The columns are typically ~5-10 nm wide. In these films the interface between the film and substrate is sharp, as can be seen from the high resolution transmission electron microscopy (HRTEM) image in Fig. 5.2.

Fig. 5.1 TEM image of a ZrB₂ thin film, with a dense and columnar structure, grown on an Al₂O₃(0001) substrate. Adapted from [49] with permission of Elsevier.

Fig. 5.2 HRTEM image of a sharp interface between the ZrB₂ film and the 4H-SiC(0001) substrate. Adapted from [50] with permission of Wiley.

For some films deposited on 4H-SiC(0001) the steps on the substrate surface results in stacking faults by causing the ZrB_2 columns to shift half a unit cell, see Fig. 5.3.

Fig. 5.3 HRTEM image of a ZrB_2 thin film grown on a 4H-SiC(0001) substrate. Adapted from [50] with permission of Wiley.

In Fig. 5.4 a Z-contrast image can be seen, showing a semi-coherent grain boundary in a ZrB_2 film deposited on $\text{Al}_2\text{O}_3(0001)$.

Fig. 5.4 Z-contrast image of a semi-coherent grain boundary in a ZrB_2 thin film grown on an $\text{Al}_2\text{O}_3(0001)$ substrate. Adapted from [49] with permission of Elsevier.

In **Paper IV** more examples of such grain boundaries are displayed. However, there are also less coherent grain boundaries where electron energy loss spectroscopy (EELS) have shown there might be a slight surplus of B atoms. For a discussion of the possible influence of these B-rich boundaries on the films' mechanical properties, see Section 5.5.2.

In addition to the films with a dense, columnar microstructure, mostly semi-coherent grain boundaries and sharp interfaces between the film and substrate, there are also films exhibiting other microstructures.

In **Paper III** the effect of sputtering power applied to the target was investigated. Films deposited at a low sputtering power of 100 W exhibit a partly columnar structure with the columns tilted somewhat in respect to the surface normal of the substrate. However, the most noticeable difference between the films grown at low sputtering power (100-200 W) and the films grown at high sputtering power (300-400 W) is the rough surface structure caused by grains growing in other directions and out of the film, see Fig. 5.5.

Fig. 5.5 TEM image exhibiting the rough surface structure of a ZrB₂ thin film grown on 4H-SiC(0001) using a sputtering power of 100 W. Adapted from [51] with permission of Elsevier.

This surface structure results in trenches and hollow spaces between the outgrowing grains where oxygen and other impurities from the atmosphere can dissolve when the sample is taken out of the UHV chamber, resulting in high levels of contaminants as discussed in Section 5.2.

For some deposition parameters on some substrate materials we have observed an amorphous layer in the interface between the film and substrate. In **Paper I** we report that films deposited without external heating on both 4H-SiC(0001) and Si(100) exhibit an amorphous or nanocrystalline layer

(~20 nm thick) at the film-substrate interface. Fig. 5.6 shows a film that has been ion-milled so that only the amorphous layer and the first few crystalline grains are seen. As stated in Section 5.2, ERDA showed that there was more oxygen in this area compared to the rest of the film. We believe that this growth behavior is due to the low mobility of the adatoms at the low deposition temperature, as well as the presence of oxygen, which hinder Zr and B on the surface to move and grains to grow.

Fig. 5.6 TEM image showing an amorphous/nanocrystalline layer at the film-substrate interface of a ZrB_2 thin film grown on a 4H-SiC(0001) substrate with no external heating.

In **Paper II** we showed that films deposited on Si(111) at a temperature of 900 °C display an uneven interface between the film and substrate, see Fig. 5.7. The wavy substrate surface suggests that the substrate has been thoroughly etched and/or that a film/substrate reaction has occurred.

Fig. 5.7 TEM image of a ZrB_2 thin film grown on a Si(111) substrate where the substrate is exhibiting a wavy interface with amorphous material in the 'valleys'.

A study by Hu et al [20], where CVD has been used to grow ZrB_2 on Si(111) at the same temperature of 900 °C, reports a smooth film-substrate interface, indicating that it is not the high deposition temperature in itself that causes the degradation. It may be due to the increased temperature caused by the energetic flux and/or the ions bombarding the surface during deposition. In the valleys of the wavy interface there is amorphous material. Energy-dispersive X-ray spectroscopy (EDX) shows that these areas consist mainly of silicon and oxygen. It is likely that it is mostly Si during the deposition process and that the oxygen is dissolved in the more porous amorphous areas after the film has been taken out of the vacuum chamber.

Sputtering ZrB_2 thin films on GaN(0001) also causes an amorphous layer to form at the film-substrate interface, see Fig. 5.8. In these films, reported on in **Paper VI**, the layer is only ~2 nm thick but this is enough to hamper the possibility of epitaxial growth, see Section 5.4. EELS and EDX measurements showed that there are B and N in the interfacial layer, but very little Zr

and Ga. The layer most likely forms as a result of the high reactivity of B with N and the reaction is eased due to decomposition of the GaN surface in vacuum at the high deposition temperature of 900 °C. Attempts were made to prevent the GaN surface of decomposing, by lowering the deposition temperature or reducing the preheating time, but they proved unsuccessful.

Fig. 5.8 TEM image showing an amorphous/nanocrystalline layer at the film-substrate interface of a ZrB_2 thin film grown on a GaN(0001) substrate.

To summarize, most of the ZrB_2 thin films deposited in this thesis exhibit a dense, columnar microstructure with a sharp film-substrate interface and with the majority of grain boundaries being semi-coherent, but there are also films where other microstructures are present, e.g. amorphous phases located at the interfaces of the film and substrate.

5.4 Film structure

Film texture, as described in Section 2, has been a focal point in the work underlying this thesis. To get as much information as possible about various aspects of the film structure, several X-ray diffraction (XRD) methods have been applied.

For diffractograms recorded for films on all substrates in this thesis, all the peaks originate from either ZrB_2 [10] or the underlying substrate, meaning that the film always consists of the ZrB_2 phase.

5.4.1 Influence of deposition temperature

In Fig. 5.9 $\theta/2\theta$ diffractograms from films deposited at different temperatures on 4H-SiC(0001) can be seen.

Fig. 5.9 $\theta/2\theta$ diffractograms from ZrB_2 films grown on 4H-SiC(0001) substrates at different deposition temperatures in the range between room temperature and 900 °C. The curves in gray are from films deposited in the industrial HV system and the curves in black are from films deposited in the UHV system. Adapted from [51,52] with permission of Elsevier.

The curves in gray are from films deposited in the industrial HV system in **Paper I** and the ones in black are from films deposited in the laboratory scale UHV system in **Paper III**. The preferred orientation changes with temperature from a 0001-orientation when no external heating is applied (RT) to a more random orientation where the $10\bar{1}1$ peak is the strongest film peak when the temperature is increased to a few hundred degrees. At even higher temperatures the orientation changes back to 0001. From the diffractograms it cannot be determined whether the

0001-oriented films are fiber textured or epitaxial. Also, it is not easy seen if the films grown at intermediate temperatures are $10\bar{1}1$ textured or if they are completely polycrystalline. To find out, pole figure measurements were conducted.

Fig. 5.10 shows pole figures for films deposited at RT, 550 °C, 600 °C, 700 °C, 820 °C, and 900 °C.

Fig. 5.10 Pole figures of ZrB_2 thin films deposited on 4H-SiC(0001) substrates at a) room temperature, b) 550 °C, c) 600 °C, d) 700 °C, e) 820 °C, and f) 900 °C. All figures are of the $10\bar{1}1$ pole except c) which is of the 0001 pole. Adapted in part from [51] with permission of Elsevier.

All pole figures are of the $10\bar{1}1$ pole except for the film deposited at 600 °C, where the investigated pole is 0001. The pole figures in Fig. 5.10 a) and b) show that the film deposited with no external

heating is 0001 fiber textured and that the film grown at 550 °C is polycrystalline. The film deposited at 600 °C, see Fig. 5.10 c), is 10 $\bar{1}$ 1 fiber textured but with some contribution from 0001-oriented grains (high intensity point in the center of the pole figure). For the films deposited at 700 °C and 820 °C, the pole figures in Fig. 5.10 d) and e), respectively, show that the structure is slowly transitioning to an 0001 epitaxial growth at higher temperatures. The high intensity in the centers of these films shows that there is a contribution from 10 $\bar{1}$ 1-oriented grains in these films which is in agreement with the $\theta/2\theta$ diffractograms in Fig. 5.9. The pole figure for the film grown at 900 °C, see Fig. 5.10 f), shows 6 distinct spots of high intensity, meaning that the film is fully epitaxial.

For films grown on Si(111), the $\theta/2\theta$ diffractograms have a more uniform appearance regardless of deposition temperature in the range 500-900 °C, see Fig. 5.11.

Fig. 5.11 $\theta/2\theta$ diffractograms from ZrB₂ films grown on Si(111) substrates at different deposition temperatures in the range between 500 °C and 900 °C.

Although when the temperature is increased the intensity of the 000 l peaks increases at the same time as the intensity of the peaks from the other ZrB₂ planes decreases. For the film deposited at 900 °C, the intensity of the 000 l peaks is lower than for the films deposited on 4H-SiC(0001) at the same temperature by a factor of 10 but the film on Si(111) is also epitaxial as seen from the pole figure in Fig. 5.16 c). In addition, the contribution from grains with other orientations are larger in the films deposited on Si(111), than in films on 4H-SiC(0001). This difference in quality

between the films grown on Si(111), compared to the films deposited on 4H-SiC(0001), we believe is due to the amorphous areas at the film-substrate interface described in Section 5.3. The difference in quality can also be seen from the reciprocal space maps (RSMs) in **paper II**. However, as reported in **Paper II** we cannot see a direct correlation between where the amorphous phase is located and where the film grows as epitaxial columns versus areas where the epitaxy is locally disrupted.

Fig. 5.12 displays $\theta/2\theta$ diffractograms for two films deposited on GaN(0001) at 500 °C and 900 °C. The GaN is grown on 4H-SiC(0001), so peaks from both GaN and SiC are seen, in addition to the ZrB₂ film peaks.

Fig. 5.12 $\theta/2\theta$ diffractograms from ZrB₂ films grown on GaN(0001) substrates at different deposition temperatures of 500 °C and 900 °C.

In contrast to the films deposited on Si(111), the $\theta/2\theta$ diffractograms for films on GaN(0001) exhibit completely different appearances at different temperatures. The 0001 peak is the strongest peak for the film grown at 900 °C, but for the film grown at 500 °C the strongest peak is 10 $\bar{1}$ 1. This is in agreement with the films grown on 4H-SiC(0001). Yet, the pole figures in Fig. 5.13 reveal that the film grown at 500 °C is polycrystalline and that the film deposited at 900 °C is 0001 fiber textured, and not epitaxial as on 4H-SiC(0001). This difference in growth behavior is attributed to the microstructure described in Section 5.3, where the GaN surface is decomposed and a thin

amorphous layer is unintentionally deposited, disrupting the potential epitaxial growth. The growth behavior on GaN(0001) is described and discussed in more detail in **Paper VI**.

Fig. 5.13 Pole figures of the $10\bar{1}1$ pole of ZrB_2 films grown on GaN(0001) at a) 500 °C and b) 900 °C.

5.4.2 Influence of sputtering power

In **Paper III** we investigated how the amount of sputtering power applied to the target influenced the film structure. The purpose was to determine whether increasing the sputtering power could be a way of increasing the mobility of the adatoms enough to achieve epitaxial growth at temperatures below 900 °C. The $\theta/2\theta$ diffractograms in Fig. 5.14 show that the contributions from grains oriented in other directions than the 0001 direction are more prominent at lower sputtering powers.

Fig. 5.14 $\theta/2\theta$ diffractograms from ZrB_2 films grown on 4H-SiC(0001) substrates at different sputtering powers between 100 W and 400 W. Reprinted from [51] with permission of Elsevier.

The pole figures in Fig. 5.15 show that although all films are epitaxial the quality deteriorates at lower sputtering powers. Thus, these results demonstrate that the sputtering power is a parameter which has a large effect on the structure of the deposited ZrB_2 films. Unfortunately, we were not able to try sputtering powers high enough to determine if a higher sputtering power would enable epitaxial growth at a lower deposition temperature. The reason for this is that using high powers require high quality targets and effective cooling of the cathode to prevent the target from cracking. This is another reason, in addition to the level of contaminants discussed in Section 5.2, why the deposition of ZrB_2 films from a compound target is a process so dependent on the availability of high quality targets.

Fig. 5.15 Pole figures of the $10\bar{1}1$ pole of ZrB_2 films grown on 4H-SiC(0001) with a sputtering power of a) 100 W, b) 200 W, c) 300 W, and d) 400 W. Reprinted from [51] with permission of Elsevier.

5.4.3 Epitaxial relationships

In Fig. 5.16 pole figures from both films and substrates can be seen for films grown on 4H-SiC(0001), Si(111), and $\text{Al}_2\text{O}_3(0001)$ and from these the epitaxial relationships between the film and substrate were determined, see Table 5.4.

Fig. 5.16 Pole figures showing a) the $10\bar{1}1$ pole of a ZrB_2 film deposited on a $4\text{H-SiC}(0001)$ substrate, and b) the $10\bar{1}1$ pole of the $4\text{H-SiC}(0001)$ substrate, c) the $10\bar{1}1$ pole of a ZrB_2 film deposited on a $\text{Si}(111)$ substrate, and d) the 220 pole of the $\text{Si}(111)$ substrate, e) the $10\bar{1}1$ pole of a ZrB_2 film deposited on a $\text{Al}_2\text{O}_3(0001)$ substrate, and f) the $10\bar{1}4$ pole of the $\text{Al}_2\text{O}_3(0001)$ substrate. Adapted from [49,50] with permission of Elsevier and Wiley.

For films grown on $4\text{H-SiC}(0001)$ there is only one epitaxial orientation, whereas for $\text{Si}(111)$ and $\text{Al}_2\text{O}_3(0001)$ there are two competing epitaxial growth directions. For the films on $\text{Si}(111)$, one direction is the majority direction, as seen by the much higher intensity of the 6 spots associated with the in-plane epitaxial relationship of $\text{ZrB}_2[11\bar{2}0] \parallel \text{Si}[10\bar{1}]$, compared to the other. For $\text{Al}_2\text{O}_3(0001)$ the sets of spots associated with the two epitaxial relationships are more or less equally strong in intensity. The two different epitaxial relationships are due to the two different

magic mismatches between the film and substrate described in Section 2.2. The in-plane epitaxial relationship of $\text{ZrB}_2[10\bar{1}0] \parallel \text{Al}_2\text{O}_3[10\bar{1}0]$ is associated with the 3:2 coincidence between Zr and Al lattices and the epitaxial relationship $\text{ZrB}_2[11\bar{2}0] \parallel \text{Al}_2\text{O}_3[10\bar{1}0]$ is associated with the 7:8 coincidence between Zr and O lattices.

Table 5.4 Epitaxial relationships for ZrB_2 films deposited on 4H-SiC(0001), Si(111), and Al_2O_3 (0001) substrates.

Substrate	Out-of-plane	In-plane 1	In-plane 2
4H-SiC(0001)	$\text{ZrB}_2(0001) \parallel 4\text{H-SiC}(0001)$	$\text{ZrB}_2[1\bar{1}00] \parallel 4\text{H-SiC}[1\bar{1}00]$	-
Si(111)	$\text{ZrB}_2(0001) \parallel \text{Si}(111)$	$\text{ZrB}_2[11\bar{2}0] \parallel \text{Si}[10\bar{1}]$	$\text{ZrB}_2[11\bar{2}0] \parallel \text{Si}[112]$
$\text{Al}_2\text{O}_3(0001)$	$\text{ZrB}_2(0001) \parallel \text{Al}_2\text{O}_3(0001)$	$\text{ZrB}_2[10\bar{1}0] \parallel \text{Al}_2\text{O}_3[10\bar{1}0]$	$\text{ZrB}_2[11\bar{2}0] \parallel \text{Al}_2\text{O}_3[10\bar{1}0]$

5.4.4 Film strain

From RSMs the lattice parameters of the deposited films can be calculated. From the lattice parameters the film strain can be evaluated according to the following equations

$$\text{In-plane strain:} \quad \varepsilon_a = \frac{a_{\text{meas}} - a_0}{a_0}$$

$$\text{Out-of-plane strain:} \quad \varepsilon_c = \frac{c_{\text{meas}} - c_0}{c_0},$$

where a_0 , c_0 are the literature values of the a and c axes and a_{meas} and c_{meas} are the corresponding measured axis values, extracted from the RSMs.

As seen from the values in Table 5.5 the lattice parameters are in rather good agreement with the literature values for bulk ZrB_2 and hence the strain in the films is low. The lowest strain is achieved for films grown on Al_2O_3 (0001). Low strain is important for films used for evaluation of mechanical properties since these measurements are known to be influenced by film strain [53].

Table 5.5 Lattice parameters and film strain values calculated from RSMs recorded for ZrB₂ films deposited on 4H-SiC(0001), Si(111), and Al₂O₃(0001) substrates.

Substrate	a [Å]	c [Å]	In-plane strain	Out-of-plane strain
Literature value (bulk) [10]	3.1687	3.5300	-	-
4H-SiC(0001)	3.174	3.518	0.0017	-0.0034
Si(111)	3.151	3.529	-0.0056	-0.0003
Al ₂ O ₃ (0001)	3.169	3.528	0.0001	-0.0005

To summarize, the temperature and sputtering power are important deposition parameters affecting the structure of sputtered ZrB₂ films. High quality epitaxial films are achieved when applying both a high deposition temperature (900 °C) and a high sputtering power (400 W). Epitaxial relationships have been determined for films grown on 4H-SiC(0001), Si(111), and Al₂O₃(0001) and the strain in these films is low. Films deposited using the same deposition parameters on GaN(0001) are fiber textured.

5.5 Film properties

5.5.1 Resistivity

The resistivity of my ZrB₂ films has been measured and reported in **Paper I-IV**. The obtained values are typically between 100 and 250 $\mu\Omega\text{cm}$. The most clear trend is that the resistivity decreases when the deposition temperature increases. We believe that this is due to reduced amounts of contaminants, especially oxygen, in films deposited at higher temperature. This theory is supported by results showing that films deposited at low sputtering power (100 W and 200 W), containing much oxygen (see Section 5.2), exhibit resistivity values of up to 500 $\mu\Omega\text{cm}$, see Fig. 5.17.

The reported literature value for ZrB₂ bulk is $\sim 8 \mu\Omega\text{cm}$ [12], so even my films with the lowest resistivity exhibit a resistivity higher than the bulk value with a factor of ~ 10 . Also, my films exhibit resistivity values higher than some CVD-grown films exhibiting values $< 50 \mu\Omega\text{cm}$ [7,22]. We speculate that this is due to higher contaminant levels in my films as well as the small width of the columns in my films affecting the resistivity due to grain boundary scattering. The resistivity of my films are lower or similar to other ZrB₂ films deposited by magnetron sputtering from a compound target [31,32,36,40,43,54].

Fig. 5.17 Resistivity values for ZrB₂ thin films grown on 4H-SiC(0001) substrates at different temperatures and sputtering powers. Reprinted from [51] with permission of Elsevier.

5.5.2 Mechanical properties

In **Paper IV** the mechanical properties of epitaxial ZrB₂ films on Al₂O₃(0001) were evaluated. The results show that the films exhibit a hardness of ~45-50 GPa, which is almost twice as high as the reported hardness values for ZrB₂ bulk (23 GPa [8]). The elastic recovery (W_e) of the films is high and was determined to between 100 % and 70 % with decreasing values for higher loads.

For other diboride thin films exhibiting superhardness (defined as ≥ 40 GPa [55]) it has been suggested that the increased hardness compared to bulk is due to the small grain size in these films, making dislocation formation unlikely, in combination with a B-rich tissue phase between the grains, hindering grain boundary sliding [56,57]. My films exhibit a large grain size in the z-direction and we believe the small grain size in the x- and y-directions is of little importance, given that my films are 0001-oriented and that the basal glide system for ZrB₂ is $\{0001\}\langle 11\bar{2}0 \rangle$. This makes dislocation movement on the 0001-planes unlikely due to the fact that no shear force is projected directly on the basal planes when the force is applied normal to these planes. We have also used EELS to investigate whether or not there is a B-rich phase between the columns. Our results indicate that there might be a small excess of B in some grain boundaries but not enough to form a B-rich tissue phase between all the columns. Instead, we propose that the main reason for the observed superhardness in my films is the 0001-orientation, causing the planes for the prismatic

glide system to be vertical just as the majority of grain boundaries in my films. This would cause the columns to move along the domain walls and be pushed down into the substrate rather than cause deformation across the columnar-like domains. This theory is supported by a TEM image after indentation of a 0001-oriented ZrB_2 thin film deposited on Si(100), see Fig. 5.18, showing that the Si substrate has been deformed whereas the ZrB_2 film looks unaffected.

Fig. 5.18 TEM image of a ZrB_2 film deposited on a Si(100) substrate at room temperature showing the mark after nanoindentation. The top part of the image is a Pt layer deposited to protect the ZrB_2 film during TEM sample preparation.

In **Paper V** *in situ* nanoindentation experiments in an inert gas environment (N_2 containing 5% H_2) at temperatures up to 600 °C were performed. The results showed that although the hardness decreased at higher temperatures for all measured samples (from 47.3 GPa at 25 °C to 32.8 GPa at 600 °C for a 0001 epitaxial film, from 30.8 GPa at 25 °C to 24.2 GPa at 600 °C for a $10\bar{1}0$ textured film, and from ~20-30 GPa at 25 °C to ~8-15 GPa at 600 °C for ZrB_2 bulk samples [58-60]) the epitaxial film exhibited higher hardness even at 600 °C than textured films and bulk samples did at 25 °C.

To summarize, my epitaxial ZrB_2 films show typical resistivity values of 100 to 250 $\mu\Omega\text{cm}$, hardness values of 45 to 50 GPa and high elastic recovery at room temperature. The elasticity and hardness is high also at elevated temperatures, compared to textured ZrB_2 films and bulk.

6 Characterization methods

6.1 X-ray diffraction

XRD is one of the most utilized characterization techniques in materials science. The reason is that the wavelength of X-rays is in the order of the distance between planes in a crystal. When a crystal is irradiated with X-rays, some of the X-rays are elastically scattered by the electrons of the atoms in the sample and constructive interference occurs according to Bragg's law

$$n\lambda = 2d_{hkl} \sin \theta$$

where n is an integer, λ the wavelength of the X-rays, d_{hkl} the distance between lattice planes with Miller indices hkl , and θ the diffraction angle. In other words the minimum requirement for constructive interference to occur is that the path difference between the diffracted beams is an integer of the wavelength of the X-rays used. Bragg's law is visualized in Fig. 6.1.

Fig. 6.1 Schematic illustration of Bragg's law.

However, not all hkl that satisfies Bragg's law will give rise to a diffraction peak; the allowed peaks are determined by the structure factor which in turn is determined by the crystal structure. The position of the peaks in a diffractogram is dependent on which atoms are present in the crystal and where they are located, giving each material its own 'fingerprint' diffractogram. Thus, XRD can be applied to confirm the identity of a material. XRD can also provide information on e.g. the orientation of the film, the crystal quality and the lattice parameters. To measure these properties several methods are applied, the three used in this thesis are described below. The notation of angles used in these methods is shown in Fig. 6.2.

Fig. 6.2 Notation of the angles in XRD.

6.1.1 $\theta/2\theta$

In a $\theta/2\theta$ scan the incident and reflected angles are always the same and both are changed simultaneously, thus $\theta/2\theta$ is a symmetrical scan. This means that only the crystal planes parallel to the sample surface will give rise to peaks in the diffraction pattern. For a completely random oriented powder sample, the different orientations of the grains ensure that all lattice planes will contribute to the diffraction pattern. In thin films it is common that a certain growth direction is more favorable, resulting in a higher intensity for the corresponding diffraction peaks. In Fig. 6.3

an example of a diffractogram with a linear scale is displayed, where the intensity of the 000 ℓ peaks are so high that those are the only visible film peaks. To be able to see whether other peaks of low intensity are present in the diffractogram it is more common to plot with a logarithmic scale, see Fig. 6.4.

Fig. 6.3 $\theta/2\theta$ diffractogram with a linear intensity scale from a ZrB_2 film grown on an $\text{Al}_2\text{O}_3(0001)$ substrate.

Fig. 6.4 $\theta/2\theta$ diffractogram with a logarithmic intensity scale from a ZrB_2 film grown on an $\text{Al}_2\text{O}_3(0001)$ substrate.

When the intensity of one diffraction peak, compared to the others, is much higher the film is either textured or epitaxial. To determine which it is, pole figure measurements can be performed.

6.1.2 Pole figures

In a pole figure the diffracted beam is fixed at one particular $\theta/2\theta$ -value, corresponding to the plane that is being investigated. The sample is then tilted in the Ψ direction and rotated in the ϕ direction and the detected intensity is plotted as a stereographic projection. The angles used in this thesis were $0 \leq \Psi \leq 85$ and $5 \leq \phi \leq 360$.

A randomly oriented film will show uniform intensity, see Fig. 6.5 a). For a textured sample where the grains are oriented in the same way out-of-plane but randomly in-plane there will be diffraction at a certain inclination angle Ψ and for all values of ϕ , resulting in a ring pattern seen in Fig. 6.5 b). If the film is epitaxial and all grains are oriented the same in-plane as well as out-of-plane, diffraction will occur only at certain values of Ψ and ϕ resulting in a pattern of distinct spots as seen in Fig. 6.5 c). The number of spots and the distance between them are determined by the symmetry of the investigated plane. The Ψ -value corresponds to the angle between the investigated plane and the planes parallel to the surface of the sample, e.g. the ring seen in Fig. 6.5 b) is located at a Ψ -value of $\sim 50^\circ$ since the angle between the investigated $10\bar{1}1$ pole and the 0001 -planes parallel to the surface in this sample is 52° .

Fig. 6.5 Pole figures of the $10\bar{1}1$ pole of a ZrB_2 film grown on a) $\text{GaN}(0001)$ at 500°C , b) $\text{GaN}(0001)$ at 900°C , and c) $4\text{H-SiC}(0001)$ at 900°C .

$\theta/2\theta$ and pole figure measurements were used extensively in all **Papers I-VI** to assess the structure of the ZrB_2 thin films and the relationships between the film and the substrate.

6.1.3 Reciprocal space maps

RSMs can be recorded to investigate a certain lattice point in reciprocal space. The shape and position of the reciprocal lattice point gives information about the in-plane and out-of-plane lattice parameters, crystal quality, strain, relaxation, and mosaicity of the films [61]. In this thesis RSMs have been recorded mainly to calculate the lattice parameters of the films and assess the film strain.

RSMs in **Paper II** were collected by performing consecutive coupled 2θ - ω scans, each with a small difference in ω -value, see Fig. 6.6. This means that the reflection is not only monitored by one measurement crossing it, but the whole area in the vicinity of the reflection is included in the measurement. For each sample one symmetric and one asymmetric Bragg reflection were investigated. In **Paper IV** 2θ scans were measured instead of 2θ - ω scans, still with a small difference in ω -value. The reason for the change was the use of another diffractometer and changing the scan direction enabled the full use of the detector, reducing the measurement time substantially.

Fig. 6.6 Schematic illustration of how a RSM is recorded by consecutive coupled 2θ - ω scans.

RSMs are plotted as diffraction intensity contours in the reciprocal space coordination system where Q_z is the out-of-plane component and Q_x is the in-plane component. An example from **Paper II**, for one symmetric and one asymmetric reflection can be seen in Fig. 6.7 a) and b), respectively.

Fig. 6.7 RSMs for a film grown on Si(111) showing a) the ZrB_2 0002 lattice point, and b) the ZrB_2 $10\bar{1}3$ lattice point. In the lower left corner the 313 lattice point from the substrate is seen. Adapted from [50] with permission of Wiley.

6.2 Electron microscopy

In EM, electrons are used to illuminate the sample in the same way as visible light in a light optical microscope (LOM). The beam is focused and the image generated with the help of electromagnetic lenses equivalent to the glass lenses in the LOM. The largest advantage of the EM, compared to

the LOM, is the improved resolution stemming from the smaller wavelength of electrons in comparison to visible light. However, whereas glass lenses have been perfected for a long time electromagnetic lenses are still of rather poor quality and limits the resolution attained. Still, LOMs are limited to a resolution of around 500 nm [62], whereas the best EM here at Linköping University can achieve a resolution of ~70 pm.

6.2.1 Scanning electron microscopy

In scanning electron microscopy (SEM) an electron probe is scanned over the surface of a sample. The electrons are accelerated to a voltage of ~1–60 keV and interact with the atoms in the sample which cause secondary electrons, backscattered electrons, Auger electrons, X-rays and visible light to be emitted from the sample. An image is generated by displaying the intensity for the selected signal, usually secondary electrons, for each position of the probe while it scans the sample. Secondary electrons have a short mean free path following their low energy, and therefore originate from the surface of the sample making them ideal for topographic imaging of the sample surface. The resolution of a SEM is ~2 nm which is lower than for TEMs. However, the SEM has other advantages including that it is a non-destructive method, requires minimal or no sample preparation and has a large depth of field making it easy to interpret an image from a 3D-shaped object.

In this thesis, SEM was used in **Paper I** to investigate the morphology of the cross-sectional films and to measure the thicknesses of the films. The obtained thicknesses were then used to calculate the deposition rate of the films by dividing the thickness with the deposition time and to calculate the resistivity of the films (see Section 6.3).

6.2.2 Transmission electron microscopy

In TEM the electrons are accelerated by a voltage of ~200-300 keV and then transmitted through the sample. This results in scattering of electrons and intensity and phase variations of the transmitted beam, holding information about the structure of the sample. TEM requires the sample to be very thin, preferably less than 50 nm thick, and the sample preparation is therefore complicated and time-consuming as well as destructive. This and the fact that it can be difficult to interpret the results are the main disadvantages of TEM. The main advantages are the high spatial resolution and the possibility to get information from both real (imaging) and reciprocal (diffraction) space. In this thesis two variations of TEM, conventional TEM (CTEM or just TEM) and scanning transmission electron microscopy (STEM), have been used.

6.2.2.1 Conventional transmission electron microscopy

In CTM the sample is illuminated by a wide electron beam and the magnification is determined by the settings of the intermediate lenses below the sample. There are a number of ways to generate contrast in a TEM image. The most common way is called bright field imaging, where 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. Areas of the sample which diffract more are imaged as darker compared to the areas where more electrons are transmitted through the sample. In dark field imaging, the aperture in the back focal plane of the objective lens is used to block the transmitted beam instead of the scattered electrons and the scattered electrons are used for imaging. In dark field images the areas that diffract more will be displayed as bright.

In HRTEM phase contrast is utilized. Both the transmitted and scattered beams are used and the path difference of the two beams gives rise to interference, thus generating contrast in the image. With HRTEM it is possible to acquire atom resolved images.

CTEM has been used in all **Papers I-VI** to get important information on the microstructure of the ZrB₂ films.

6.2.2.2 Scanning transmission electron microscopy

In STEM the electron beam is focused to a probe which is scanned over the sample and the magnification achieved is determined by the size of the area scanned by the probe. The most common detector used in STEM is high-angle annular dark field where the contrast is generated by differences in mass of the atoms and thickness variations of the sample (usually called Z-contrast). STEM was used in **Paper IV** to get high resolution images of semi-coherent grain boundaries as well as in **Paper VI** to investigate the amorphous layer at the interface of the ZrB₂ film and the GaN(0001) substrate.

6.2.2.3 Selected area electron diffraction

In TEM a diffraction pattern is formed when the electron beam is diffracted by the atoms in the sample and Bragg's law is fulfilled, in a similar way as in XRD. The pattern is formed in the back focal plane of the objective lens, and by changing the strength of the intermediate lens the diffraction pattern can be imaged instead of the ordinary image. An aperture inserted in the image plane of the objective lens makes it possible to choose a beam from a limited part of the sample, so called selected area electron diffraction (SAED) and thus obtain crystallographic information

from just one grain or another small area of interest. SAED was used in all **Papers I-VI** to evaluate the texture of the films to support the findings from XRD pole figures.

6.3 Resistivity measurements

The resistivity of a thin film can be measured with a four-point probe. Fig. 6.8 shows a schematic illustration of a four point probe pressed against the surface of a thin film.

Fig. 6.8 Schematic illustration of the set-up for a four-point probe.

One pair of the probe measures the current and the other pair the voltage. From this the sheet resistance R_s of a thin sheet can be obtained from

$$R_s = \frac{\pi}{\ln 2} \frac{V}{I} = 4.532 \frac{V}{I}$$

where I is an applied current and V is the measured voltage. This equation is valid for $t \leq s/2$ where t is the thickness of the film and s is the distance between probes. For the instruments used in this thesis the sheet resistance R_s is obtained from the instrument directly. The sheet resistance is then multiplied with the film thickness t (obtained from SEM) in cm to get the specific resistivity ρ of the film in Ωcm according to

$$\rho = R_s \times t$$

Four-point probe measurements were performed to measure the resistivity of the films in **Paper I**, **Paper III**, and **Paper IV**.

6.4 Composition analysis

6.4.1 Elastic recoil detection analysis

ERDA is a quantitative as well as qualitative ion beam technique used to analyze the chemical composition and level of contaminants in a film. A beam of heavy ions with high energy is used to ‘kick out’ or recoil atoms from the film in the forward direction. In **Paper I** the measurements were carried out using a 36 MeV $^{127}\text{I}^{8+}$ ion beam and the incident angle was such that the recoil angle was 45° . The energy of the ejected atoms is measured and since the collision is assumed to be fully elastic the mass of the target atom can be calculated from the kinematic factor k_{ER} according to

$$k_{ER} = \frac{E_R}{E_p} = \frac{4M_p \times M_R}{(M_p + M_R)^2} \cos^2 \theta$$

where E_p and M_p is the energy and mass of the projected ion, respectively, E_R and M_R is the energy and mass of the recoiled atom, respectively, and θ is the recoil angle. The energy of the ejected atoms is dependent on the depth of their origin in the film. In **Paper I** ToF-ERDA was used where, in addition to the energy of the atoms, their velocity is measured to be able to determine both the mass of the ejected atoms, but also enabling depth profiles of the elements in the film. Depth profiles enabled us to see that the oxygen content in the films was higher at the film-substrate interface compared to the bulk of the film.

ERDA is best suitable for light elements and it is possible to measure hydrogen, which is an advantage compared to many other techniques.

6.4.2 X-ray photoelectron spectroscopy

XPS is a technique based on the photoelectric effect. XPS provides information about the chemical composition and the bonding structure of a sample. In XPS an X-ray beam is used to irradiate a sample. The known photon energy (in this thesis 1486.6 eV) is transferred to a core electron of an atom in the sample which is emitted from the sample. An electron emitted in this way is called a photoelectron. The kinetic energy E_{kin} of the photoelectron is measured and depends on the photon energy $h\nu$, the binding energy of the electron E_B , and the work function ϕ (energy needed to leave the sample) according to

$$h\nu = E_B + E_{kin} + \phi_{sample}$$

However, the measured kinetic energy E'_{kin} actually depends on the work function of the spectrometer and not the work function of the sample (see Fig. 6.9).

Fig. 6.9 Schematic illustration of the energy levels interesting for XPS analysis.

The work function of the spectrometer can be measured using a control sample and is thus a known variable. Hence, E_B can be obtained from the following equation

$$E_B = h\nu - E'_{kin} - \phi_{spec}$$

E_B is element specific but also depends on the chemical environment of the atom, i.e. which other atoms/group of atoms the source atom binds to. Depending on whether the atom is bonded to a more electronegative or electropositive atom/group of atoms E_B will shift slightly. These chemical shifts are used to assess the bonding structure in the sample.

XPS is a surface sensitive method since the inelastic mean free path of the emitted photoelectron is ~5-10 nm. This is the reason why XPS is performed in UHV. Since the technique is so surface sensitive and there is always contaminants on a sample surface, the sample is usually sputter cleaned using noble gas ions (in this thesis Ar ions) before measurement. Sputter etching can also be used to perform depth profiles to obtain information about the composition and bonding structure of a sample at different thicknesses. The intensity of the photoelectrons with a certain E_B is related to the amount of the corresponding element in the sample, but sensitivity factors obtained

from samples with known composition are needed to make a quantitative evaluation of the sample composition.

In **Paper III** XPS was used to determine the composition of ZrB_2 thin films deposited on 4H-SiC(0001) at different temperatures and when applying different amounts of power to the target. Peaks in the spectrum, recorded from an as-deposited film grown at 900 °C, originating from bonds between oxygen and either Zr or B were not observed after sputter cleaning of the surface, meaning that most of the oxygen was present in the form of a thin surface oxide, see Fig. 6.10.

Fig. 6.10 High resolution XPS spectra of the Zr 3d and B 1s photoelectron region from a ZrB_2 film deposited at 900 °C and with 400 W applied to the target. The dotted line represents the as deposited film and the solid line is after 180 s of sputter cleaning. Reprinted from [51] with permission of Elsevier.

6.4.3 Energy-dispersive X-ray spectroscopy

As stated in Section 6.2.1, electrons in an electron microscope interact with the atoms in the sample, causing secondary electrons, backscattered electrons, Auger electrons, X-rays, and visible light to be emitted from the sample. In EDX the emitted X-rays are utilized to gain information on the chemical composition of the sample. The principle is that the electron beam excites a core electron in an atom, ejecting the electron from the sample, thus creating an electron hole. An electron from a higher binding energy level in the atom then fills the hole and the energy difference between the two states can be released as X-rays. The energy difference of the two states, and thus the energy of the emitted X-rays, is characteristic for each element. The number and energy of the emitted X-rays can be measured by an energy-dispersive X-ray spectrometer, allowing the elemental

composition of the sample to be evaluated. EDX is best suited for heavier elements since the probability of emitting X-rays is lower for lighter elements.

EDX can be used to assess the elemental distribution over a surface by recording an EDX spectrum for each image point in an electron microscope image. It is then possible to visualize the intensity changes in a specific energy area, corresponding to each element, with a color, e.g. in Fig. 6.11 where the intensity of the area of the Zr peak is red and the area of the Ga peak is green. This technique is called EDX spectrum imaging and the ‘maps’ of each element are then superimposed on the micrograph. In **Paper VI** EDX mapping was applied to investigate the distribution of elements at the film-substrate interface, and an example of a map showing the distribution of Ga and Zr is shown in Fig. 6.11.

Fig. 6.11 Z-contrast image with superimposed EDX maps showing Zr (red) and Ga (green).

6.4.4 Electron energy loss spectroscopy

When high-energy electrons interact with a sample, some of the electrons lose part of their E_{kin} . EELS is a technique which measures this loss of E_{kin} for the inelastically scattered electrons in an electron microscope. Both elemental composition and atomic bonding states can be determined by EELS. An EELS spectrum can be recorded for each point in a STEM image and the signals can then be averaged over a given area of interest, enabling evaluation of very distinct regions in the sample.

In **Paper IV** EELS was used to evaluate whether or not we had segregated B in the grain-boundaries by comparing EELS spectra from the center of a grain with spectra from the grain-boundaries. In **Paper VI** EELS mapping was applied to investigate the amorphous

intermediate layer at the film-substrate interface. The energy resolution possible with the TEM used in **Paper IV** and **Paper VI** is 0.2 eV at an acceleration voltage of 300 kV.

6.5 Nanoindentation

Evaluation of the mechanical properties of a thin film is challenging since it is important that the measured properties originates from the film, and not the much thicker substrate. Nanoindentation is a commonly used method where 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. One indentation consists of three parts. First the loading part where the load is measured until it reaches the maximum applied load, second a hold part where the applied load is held for a time to monitor drift, and third the unloading part where the load is decreased gradually to zero. The result is a load-displacement curve, see Fig. 6.12.

Fig. 6.12 Load-displacement curve recorded from a ZrB_2 film deposited on $\text{Al}_2\text{O}_3(0001)$.

From the load-displacement curve the hardness and the reduced Young's modulus E_r can be obtained by applying the method developed by Oliver and Pharr [63].

The hardness of a material is defined as its resistance to plastic deformation. In nanoindentation the hardness is calculated according to

$$Hardness = \frac{L_{max}}{A}$$

where L_{max} is the maximum applied load and A is the contact area of the tip. A is dependent on the geometry of the tip (in this thesis a pyramid shaped Berkovich tip) and the contact depth h_c retrieved from the load-displacement curve. E_r is extracted from the shape of the unloading part of the load-displacement curve (see Fig. 6.12) according to

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A}} \left(\frac{dL}{dh} \right)$$

In **Paper IV** both the hardness and E_r for ZrB_2 thin films grown on $Al_2O_3(0001)$ were reported. In addition, the W_e of these films was evaluated. W_e is a measurement of how much of the total deformation is recovered as elastic strain upon release of the load. W_e is calculated as

$$W_e = 100 \times \frac{(h_{max} - h_f)}{h_{max}}$$

where h_{max} is the maximum penetration depth (produced at the maximum indentation load) and h_f corresponds to the final displacement after complete unloading.

In **Paper V** the hardness, E_r and W_e were evaluated at elevated temperatures up to 600 °C for ZrB_2 films deposited on $SiC(0001)$ and $Si(100)$.

7 Conclusions

In this thesis I have demonstrated that it is possible to deposit stoichiometric ZrB_2 thin films with low levels of impurities from a compound target using DCMS. Epitaxial growth was achieved on 4H-SiC(0001), Si(111), and Al_2O_3 (0001) substrates, while growth on GaN(0001) templates resulted in polycrystalline or textured films.

Parameters found crucial for the crystal quality of the films were deposition temperature and sputtering power, where values of 900 °C and 400 W (on a 3 inch target), respectively, resulted in the highest quality films.

The epitaxial films exhibit typical resistivity values of ~100-250 $\mu\Omega\text{cm}$ which are similar to other magnetron sputtered ZrB_2 films, high hardness values of 45-50 GPa and high elastic recovery.

The mechanical properties of epitaxial films are also retained to a higher degree at high temperatures, compared to textured ZrB_2 thin films and bulk.

8 Future outlook

The high crystal quality of the ZrB_2 films deposited in this thesis has made them interesting as templates for growth of semiconductor BP films as well as for template growth of GaN nanorods and collaborations have started on these projects. These applications are enabled from the good lattice match of ZrB_2 to BP and GaN. In the future it will be interesting to see whether sputtered ZrB_2 thin films will be used as templates also for other materials with appropriate lattice matches, such as silicene [19].

For improving the quality of sputtered ZrB_2 films further, I see two alternatives

- Continue working with compound targets and test higher temperatures and higher sputtering powers.
- Investigate possible B precursors for the development of reactive sputtering processes.

The second alternative would eliminate the dependence of the availability of high quality compound targets and is therefore probably preferable to the first alternative. Some initial studies on possible alternatives to B_2H_6 as a B precursor to reactively sputter ZrB_2 thin films is ongoing. An attempt using $\text{B}(\text{CH}_3)_3$ resulted in ZrC films (unpublished results). BF_3 has previously been used to sputter TiB_2 [64] and shows promising preliminary results for deposition of ZrB_2 films as well.

It has been showed that annealing of amorphous ZrB_2 films, deposited by e-beam evaporation, decreases their resistivity due to grain growth [65]. Annealing of sputtered epitaxial ZrB_2 films should be investigated to see if the column width increases and the resistivity decreases.

References

- [1] Lundström T. Transition metal borides. In: Boron and Refractory Borides, Springer, 1977. p. 351.
- [2] Fahrenholtz WG, Wuchina EJ, Lee WE, & Zhou Y. Ultra-high temperature ceramics: materials for extreme environment applications. John Wiley & Sons, 2014.
- [3] Pallas A, Larsson K. Structure determination of the 4D metal diborides: A quantum mechanical study, J. Phys. Chem. B 2006;110:5367.
- [4] Vajeeston P, Ravindran P, Ravi C, Asokamani R. Electronic structure, bonding, and ground-state properties of AlB_2 -type transition-metal diborides, Phys. Rev. B 2001;63:045115.
- [5] Massalski, TB, Murray, JL, Bennett, LH, Baker, H. Binary Alloy Phase Diagrams 1986
- [6] Tolle J, Roucka R, Tsong IST, Ritter C, Crozier PA, Chizmeshya AVG, Kouvetakis J. Epitaxial growth of group III nitrides on silicon substrates via a reflective lattice-matched zirconium diboride buffer layer, Appl. Phys. Lett. 2003;82:2398.
- [7] Bera S, Sumiyoshi Y, Yamada-Takamura Y. Growth of single-crystalline zirconium diboride thin film on sapphire, J. Appl. Phys. 2009;106:063531-1.
- [8] Fahrenholtz WG, Hilmas GE, Talmy IG, Zaykoski JA. Refractory diborides of zirconium and hafnium, J. Am. Ceram. Soc. 2007;90:1347.
- [9] Maruska HP, Tietjen JJ. The preparation and properties of vapor-deposited single-crystalline GaN, Appl. Phys. Lett. 1969;15:327.
- [10] JCPDS- International Centre for Diffraction Data. Zirconium diboride (ZrB_2) Ref ID 00-034-0423
- [11] Motojima S, Funahashi K, Kurosawa K. ZrB_2 coated on copper plate by chemical vapour deposition, and its corrosion and oxidation stabilities, Thin Solid Films 1990;189:73.

- [12] Rahman M, Wang CC, Chen W, Akbar SA, Mroz C. Electrical Resistivity of Titanium Diboride and Zirconium Diboride, *J. Am. Ceram. Soc.* 1995;78:1380.
- [13] Desai PD, James HM, Ho CY. Electrical resistivity of vanadium and zirconium, *J. Phys. Chem. Ref. Data* 1984;13:1097.
- [14] JCPDS- International Centre for Diffraction Data. Silicon carbide (SiC) Ref ID 00-029-1127
- [15] JCPDS- International Centre for Diffraction Data. Gallium nitride (GaN) Ref ID 00-076-0703
- [16] Pierson HO. Handbook of refractory metal carbides and nitrides. New Jersey: Noyes publications, 1996.
- [17] Stross EK. The refractory metal carbides. New York: Academic Press, 1967.
- [18] Fleurence A, Yamada-Takamura Y. Scanning tunneling microscopy investigations of the epitaxial growth of ZrB₂ on Si(111), *Phys. Status Solidi C* 2011;8:779.
- [19] Fleurence A, Friedlein R, Ozaki T, Kawai H, Wang Y, Yamada-Takamura Y. Experimental evidence for epitaxial silicene on diboride thin films, *Phys. Rev. Lett.* 2012;108:245501-1.
- [20] Hu C-W, Chizmeshya AVG, Tolle J, Kouvetakis J, Tsong IST. Nucleation and growth of epitaxial ZrB₂(0 0 0 1) on Si(1 1 1), *J. Cryst. Growth* 2004;267:554.
- [21] Roucka R, Tolle J, Chizmeshya AVG, Tsong IST, Kouvetakis J. Epitaxial film growth of zirconium diboride on Si(001), *J. Cryst. Growth* 2005;277:364.
- [22] Sung J, Goedde DM, Girolami GS, Abelson JR. Remote-plasma chemical vapor deposition of conformal ZrB₂ films at low temperature: A promising diffusion barrier for ultralarge scale integrated electronics, *J. Appl. Phys.* 2002;91:3904.
- [23] Tolle J, Kouvetakis J, Kim D-W, Mahajan S, Chizmeshya AVG, Hu C-W, Bell A, Ponce FA, Tsong IST. Epitaxial growth of ZrB₂(0001) on Si(111) for III-nitride applications: A review, *Chin. J. Phys.* 2005;43:233.
- [24] Wayda AL, Schneemeyer LF, Opila RL. Low-temperature deposition of zirconium and hafnium boride films by thermal decomposition of the metal borohydrides (M[BH₄]₄), *Appl. Phys. Lett.* 1988;53:361.
- [25] Ferrando V, Tarantini C, Pallecchi I, Ferdeghini C, Manfrinetti P, Salvato M. Growth of diborides thin films on different substrates by pulsed laser ablation, *Thin Solid Films* 2006;515:1439.

- [26] Rau JV, Ferro D, Falcone MB, Generosi A, Albertini VR, Latini A, Teghil R, Barinov SM. Hardness of zirconium diboride films deposited on titanium substrates, *Mater. Chem. Phys.* 2008;112:504.
- [27] Stewart DM, Meulenberg RW, Lad RJ. Nanostructure and bonding of zirconium diboride thin films studied by X-ray spectroscopy, *Thin Solid Films* 2015;596:155.
- [28] Stewart DM, Frankel DJ, Lad RJ. Growth, structure, and high temperature stability of zirconium diboride thin films, *J. Vac. Sci. Technol. A* 2015;33:031505-1.
- [29] Lee D, Sim G, Xiao K, Vlassak JJ. Low-Temperature Synthesis of Ultra-High-Temperature Coatings of ZrB₂ Using Reactive Multilayers, *J. Phys. Chem. C* 2014;118:21192.
- [30] Brandstetter E, Mitterer C, Ebner R. A transmission electron microscopy study on sputtered Zr-B and Zr-B-N films, *Thin Solid Films* 1991;201:123.
- [31] Chakrabarti UK, Barz H, Dautremont-Smith WC, Lee JW, Kometani TY. Deposition of zirconium boride thin films by direct current triode sputtering, *J. Vac. Sci. Technol. A* 1987;5:196.
- [32] Guziewicz M, Piotrowska A, Kamińska E, Gołaszewska K, Turos A, Mizera E, Winiarski A, Szade J. Characteristics of sputter-deposited TiN, ZrB₂ and W₂B diffusion barriers for advanced metallizations to GaAs, *Solid-State Electron.* 1999;43:1055.
- [33] Ignatenko PI, Terpii DN, Goncharov AA. Phase composition of films deposited by ZrB₂ RF magnetron sputtering, *Inorg. Mater.* 2003;39:464.
- [34] Jouanny I, Palisaitis J, Ngo C, Mayrhofer P, Hultman L, Persson PÅ, Kodambaka S. In situ transmission electron microscopy studies of the kinetics of Pt-Mo alloy diffusion in ZrB₂ thin films, *Appl. Phys. Lett.* 2013;103:121601.
- [35] Kelesoglu E, Mitterer C, Kazmanli MK, Ürgen M. Microstructure and properties of nitride and diboride hard coatings deposited under intense mild-energy ion bombardment, *Surf. Coat. Technol.* 1999;116–119:133.
- [36] Lee C-T, Chiang D, Chen W-C, Chiu P-K, Su C-Y. Effect of substrate temperature on the properties of ZrB₂ film on Si(111) deposited by pulsed DC magnetron sputtering, *JPN J. Appl. Phys.* 2014;53:095503-1.
- [37] Meng Y, Ma F, Song Z, Li Y, Xu K. Nano-grained ZrB₂ thin films as a high-performance diffusion barrier in Cu metallization, *RSC Adv.* 2016;6:844.
- [38] Mitterer C, Ubleis A, Ebner R. Sputter deposition of wear-resistant coatings within the system Zr-B-N, *Mater. Sci. Eng. A* 1991;140:670.

- [39] Mitterer C, Komenda-Stallmaier J, Losbichler P, Schmölz P, Werner WSM, Störi H. Sputter deposition of decorative boride coatings, *Vacuum* 1995;46:1281.
- [40] Shappirio JR, Finnegan JJ. Synthesis and properties of some refractory transition metal diboride thin films, *Thin Solid Films* 1983;107:81.
- [41] Shappirio JR, Finnegan JJ, Lux RA, Fox DC. Resistivity, oxidation kinetics and diffusion barrier properties of thin film ZrB_2 , *Thin Solid Films* 1984;119:23.
- [42] Sun Y, Xiao X, Chai G, Xu G, Xiong B, Zhang S. Microstructure, optical properties and thermal stability of ZrB_2 and Zr-B-N thin films as high-temperature solar selective absorbers, *Mater. Express* 2014;4:205.
- [43] Takeyama MB, Noya A, Nakadai Y, Kambara S, Hatanaka M, Hayasaka Y, Aoyagi E, Machida H, Masu K. Low temperature deposited Zr-B film applicable to extremely thin barrier for copper interconnect, *Appl. Surf. Sci.* 2009;256:1222.
- [44] Forsberg U, Lundskog A, Kakanakova-Georgieva A, Ciechonski R, Janzén E. Improved hot-wall MOCVD growth of highly uniform $\text{AlGaIn}/\text{GaIn}/\text{HEMT}$ structures, *J. Cryst. Growth* 2009;311:3007.
- [45] Larsson T, Blom H-O, Berg S, Östling M. Reactive sputtering of titanium boride, *Thin Solid Films* 1989;172:133.
- [46] Helmersson U, Lättemann M, Bohlmark J, Ehasarian AP, Gudmundsson JT. Ionized physical vapor deposition (IPVD): A review of technology and applications, *Thin Solid Films* 2006;513:1.
- [47] Ohring M. *Materials Science of Thin Films*. Academic Press, 2002.
- [48] Oder TN, Martin P, Adedeji AV, Isaacs-Smith T, Williams JR. Improved schottky contacts on n-type 4H-SiC using ZrB_2 deposited at high temperatures, *J. Electron. Mater.* 2007;36:805.
- [49] Tengdelius L, Broitman E, Lu J, Eriksson F, Birch J, Nyberg T, Hultman L, Högberg H. Hard and elastic epitaxial ZrB_2 thin films on $\text{Al}_2\text{O}_3(0001)$ substrates deposited by magnetron sputtering from a ZrB_2 compound target, *Acta Mater.* 2016;111:166.
- [50] Tengdelius L, Birch J, Lu J, Hultman L, Forsberg U, Janzén E, Högberg H. Magnetron sputtering of epitaxial ZrB_2 thin films on 4H-SiC(0001) and Si(111), *Phys. Status Solidi A* 2014;211:636.
- [51] Tengdelius L, Greczynski G, Chubarov M, Lu J, Forsberg U, Hultman L, Janzén E, Högberg H. Stoichiometric, epitaxial ZrB_2 thin films with low oxygen-content deposited by magnetron sputtering from a compound target: Effects of deposition temperature and sputtering power, *J. Cryst. Growth* 2015;430:55.

- [52] Tengdelius L, Samuelsson M, Jensen J, Lu J, Hultman L, Forsberg U, Janzén E, Högberg H. Direct current magnetron sputtered ZrB₂ thin films on 4H-SiC(0001) and Si(100), *Thin Solid Films* 2014;550:285.
- [53] Tsui T, Oliver W, Pharr G. Influences of stress on the measurement of mechanical properties using nanoindentation: Part I. Experimental studies in an aluminum alloy, *J. Mater. Res.* 1996;11:752.
- [54] Samuelsson M, Jensen J, Helmersson U, Hultman L, Högberg H. ZrB₂ thin films grown by high power impulse magnetron sputtering from a compound target, *Thin Solid Films* 2012;526:163.
- [55] Veprek S. The search for novel, superhard materials, *J. Vac. Sci. Technol. A* 1999;17:2401.
- [56] Mayrhofer PH, Mitterer C, Wen JG, Greene JE, Petrov I. Self-organized nanocolumnar structure in superhard TiB₂ thin films, *Appl. Phys. Lett.* 2005;86:131909-1.
- [57] Nedfors N, Tengstrand O, Lu J, Eklund P, Persson POA, Hultman L, Jansson U. Superhard NbB_{2-x} thin films deposited by dc magnetron sputtering, *Surf. Coat. Technol.* 2014;257:295.
- [58] Bsenko L, Lundström T. The high-temperature hardness of ZrB₂ and HfB₂, *J. Less Common Met.* 1974;34:273.
- [59] Nakano K, Matsubara H, Imura T. High-temperature hardness of iva-diborides single crystals, *J. Less Common Met.* 1976;47:259.
- [60] Xuan Y, Chen Cu, Otani S. High temperature microhardness of ZrB₂ single crystals, *J. Phys. D* 2002;35:L98.
- [61] Birkholz M. *Thin Film Analysis by X-Ray Scattering*. Weinheim, Germany: WILEY-VCH Verlag GmbH & Co, 2006.
- [62] Pedrotti FL, & Pedrotti LS. *Introduction to Optics*. Prentice-Hall, Inc, 1993.
- [63] Oliver WC, Pharr GM. Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology, *J. Mater. Res.* 2004;19:3.
- [64] Padmanabhan K, Sørensen G. The effect of ion implantation on rf-sputtered TiB₂ films, *Thin Solid Films* 1981;81:13.
- [65] Zagozdzon-Wosik W, Rusakova I, Darne C, Zhang Z-H, Van Der Heide P, Majhi P. Microstructure and electrical properties of diborides modified by rapid thermal annealing, *J. Microsc.* 2006;223:227.

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