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Cover image: The in-plane distribution of Zr in a 20 nm thick atom probe tomography ion map of $\text{ZrB}_{2.5}$, where each dot represents a Zr ion.

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Hard ceramic thin films, including TiSiN, ZrAlN, ZrB₂, and ZrTaB₂, with applications for wear-resistant coatings, have been studied using atom probe tomography and correlated with several other analytical techniques, including X-ray diffraction, electron microscopy, and elastic recoil detection analysis. Outstanding obstacles for quantitative atom probe tomography of ceramic thin films have been surmounted.

Mass spectral overlaps in TiSiN, which make ²⁸Si indistinguishable from ¹⁴N, was resolved by isotopic substitution with ¹⁵N, and the nanostructural distribution of elements was thus revealed in 3-D, which enabled the identification of additional structural elements within the nanostructured Ti_{0.81}Si_{0.19}¹⁵N film. Improvements to the growth model of TiSiN by cathodic arc deposition was suggested.

A self-organized nanolabyrinthine structure of ZrAlN, consisting of standing lamellae of fcc-ZrN and hexagonal AlN, was investigated with focus on the onset and limits of the self-organization. The local crystallographic orientational relationships were (001)_{ZrN} || (0001)_{AlN} and <110>_{ZrN} || <2-1-10>_{AlN}. Close to the MgO substrates, a smooth transition region was formed, going from segregated and disordered to the self-organized nanolabyrinthine structure. With increased growth temperature, coarse (111)-oriented ZrN grains occasionally precipitated and locally replaced the nanolabyrinthine structure. Significant local magnification effects rendered the Zr and N signals unusable, thereby inhibiting quantitative compositional analysis of the constituent phases, but the nanostructure was resolved using the Al signal.

Ceramic materials are often affected by correlated evaporation, which can result in losses due to the detector dead-time/space. A compositional correction procedure was suggested, tested against an established procedure, and applied to ZrB₂. The correction was found to be less dependent on the isotope abundances and background correction compared to the established procedure. While losses due to dead-time/space occur in atom probe tomography of all materials, the correlative field evaporation behavior of ceramics significantly increases the compositional error. The evaporation behavior of ZrB₂ was therefore thoroughly investigated and evidence of preferential retention, correlated evaporation, and inhomogeneous field distributions at a low-index pole was presented. The high mass resolution, relatively low multiple events percentage, and quality of the co-evaporation correlation data was partly attributed to the crystal structure and film orientation, which promoted a layer-by-layer field evaporation.

The evaporation behavior of the related Zr_{0.8}Ta_{0.2}B_{1.8} film was found to be similar to that of ZrB₂. The distribution of Ta in relation to Zr was investigated, showing that the column boundaries were both metal- and Ta-rich, and that there was a significant amount of Ta in solid solution within the columns. The addition

of Ta and the resulting metal-rich boundaries increased both the hardness and toughness, compared to the $\text{ZrB}_{2.4}$ reference sample.

In addition, an instrumental artefact previously not described in atom probe tomography was found in several of the materials investigated in this thesis. The artefact consists of high-density lines along the analysis direction, which cannot be related to pole artefacts. The detection system of the atom probe was identified as the cause, because the artefact patterns on detector histograms coincided with the structure of the microchannel plate. Inconsistencies in the internal boundaries of the microchannel plate multifibers from the manufacturing process can influence the signal to the detector and locally increase the detection efficiency in a pattern characteristic to the microchannel plate in question.

Altogether, this thesis shows that atom probe tomography of nitride and boride thin films is burdened by several artefacts and distortions, but that relevant material outcomes can nevertheless be achieved by informed choices of film isotopic constituents and analytical parameters, as well as exclusion of heavily distorted regions (such as pole artefacts), and the use of compositional correction procedures when applicable.

POPULÄRVETENSKAPLIG SAMMANFATTNING

I denna doktorsavhandling undersöks hur olika parametrar, exempelvis ämnessammansättning eller tillväxttemperatur, ger upphov till strukturer inom hårda keramiska ytskikt på en skala från nanometer till mikrometer. Dessa strukturer påverkar på ett avgörande sätt ytskiktens egenskaper och prestanda. En viktig del av avhandlingen är metodutveckling för att anpassa mättekniken atomsondstomografi och efterföljande behandling av data till analys av keramiska ytskikt. Med denna teknik har till och med atomär upplösning demonstrerats för vissa keramiska prover under speciella förhållanden.

Ytskikt, eller så kallade tunna filmer, kan variera i tjocklek från ett atomlager upp till någon mikrometer. Det är grunden för en typ av materialdesign som används i snabbt växande omfattning i olika konsumentprodukter, både av estetiska och tekniska anledningar. Genom att belägga ett tjockare material (substrat) med ett väl valt ytskikt kan fördelaktiga egenskapskombinationer uppstå, som i sin tur resulterar i drastiskt förbättrad prestanda. Några vanliga tillämpningar är så kallade non-stick-beläggningar som förhindrar att mat bränner fast i stekpannor, genomskinliga anti-reflektionsfilmer på glasögonlinser och inte minst för att halvledarelektroniken, som mobiltelefoner och datorer bygger på, ska fungera.

Avhandlingen berör främst hårda tunna filmer som används, eller kan användas, som skyddsbarriär på verktyg för skärande bearbetning, som borrar, fräsning eller svarvning av metall. Ett hårt material är också ofta sprött, likt glas. Genom att belägga ett relativt segt substrat, till exempel en metall, med ett hårt ytskikt kan man kombinera dessa egenskaper. Ett hårt verktyg med en seg kärna kan användas under en längre tid, eller vid högre temperaturer, innan det måste bytas ut. Genom att undersöka filmer som har gjorts under olika förutsättningar, som temperatur eller ämnessammansättning, kan man dra slutsatser kring hur materialets strukturer uppstår och därmed hur man bör belägga materialet för att förbättra olika egenskaper.

I detta verk har flera materialvetenskapliga analysmetoder, bland annat röntgendiffraktion, transmissionselektronmikroskopi och atomsondstomografi, använts för att undersöka hur olika keramiska material är uppbyggda på nanometerskala. Atomsondstomografi, en teknik där man mäter en liten spets av det material man är intresserad av atom för atom och sedan skapar en virtuell avbildning i tre dimensioner, en så kallad rekonstruktion, har varit central för forskningen här. De allmänt tillämpade rekonstruktionsmetoderna utgår från att joniserade atomer (som saknar en eller flera elektroner) lämnar spetsen en i taget under kontrollerade former, så att spetsens yta alltid är jämn. Detta stämmer dock sällan för keramiska prover. De starka bindningarna mellan vissa ämnen i keramer gör att dessa atomer ofta lämnar spetsen som en grupp joner, istället för en och en, vilket påverkar deras positioner i rekonstruktionen. Eftersom

detektorn ibland räknar för få joner när de lämnar spetsen i grupp, kommer ämnen som huvudsakligen lämnar spetsen en och en dessutom att bli över-representerade, medan det mäts för lite av de ämnen som lämnar spetsen i grupp. För många material är skillnaden i sammansättning mindre än den som uppstår på grund av andra felkällor, men för keramer är den ofta det största mätfelet. Vid tidigare mätningar med dessa mätfel har en metod för att korrigera sammansättningen ibland använts. Resultatet av korrigeringen är dock starkt beroende av att atomsondmätningens bakgrundskorrigering är tillräckligt bra, samt att fördelningen mellan de analyserade ämnenas olika isotoper har uppmätts eller kan antagas vara nära de normalvärden som tidigare har bestämts. Isotoper av ett grundämne har olika antal neutroner i atomkärnan, och har därför olika massa, men är i övrigt väldigt lika. I denna avhandling görs en innovativ vidareutveckling av metoden, som gör korrektionen oberoende av bakgrundskorrigering och betydligt mindre känslig för isotopsammansättningen.

Atomsondstomografi har i vissa fall även svårt att skilja på ämnen vars massa korrelerar, till exempel att skilja kvävejoner från de dubbelt så tunga kiseljonerna. För att atomsonden ska kunna skilja kväve från kisel i de tunna filmerna produceras dessa med hjälp av tungt kväve, en isotop av kväve som har en extra neutron per atomkärna jämfört med den vanligaste varianten av kväve. Med hjälp av det tunga kvävet kunde en nya delar av en struktur upptäckas, vilket bidrar till beskrivningen av hur strukturerna skapas när filmen beläggs.

Avhandlingen berör även upptäckten av en ny artefakt, ett systematiskt fel, som inte har beskrivits tidigare inom atomsondstomografi. Vanliga skador från när en särskild komponent i detektionssystemet tillverkas visar sig kunna ge skillnader i hur stor andel av alla joner som detektorn kan upptäcka, beroende på var på detektorn jonerna träffar. När tillräckligt många joner har registrerats av detektorn blir ett mönster synligt och detta mönster är karaktäristiskt för den skadade komponenten.

Avhandlingen handlar alltså såväl om att beskriva strukturen i de undersökta ytskikten, som hur man bör använda atomsonden när keramiska material undersöks, samt hur man kan kompensera eller ta hänsyn till de eventuella fel som uppstår.

PREFACE

This Thesis is the result of my doctoral studies in the field of materials science, in particular thin film physics. It covers the most important parts of my research in the Thin Film Physics Division at the Department of Physics, Chemistry, and Biology (IFM) at Linköping University, Sweden. The key results of my studies are found in the appended Papers; some of which have been published in peer-reviewed scientific journals. The introductory chapters are based on my licentiate thesis *Atom Probe Tomography of TiSiN Thin Films*, Linköping Studies in Science and Technology. Licentiate Thesis. No 1733, 2015.

Part of the work has been conducted within Theme 2 of the VINN Excellence Center Functional Nanoscale Materials (FunMat), in collaboration with Sandvik Coromant, SECO Tools and Ionbond Sweden.

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

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To my friends and family for always being there, and especially for your support when life dealt me a bad hand. The person I am today is as much a result of your strength and persistence, as my own.

Nevertheless, the greatest of thanks goes to my wife **Linda**, for the hard work and sacrifices she has made to make us a family, and to my beloved children **Freja** and **Otto**, for brightening my day – every day.

LIST OF INCLUDED PAPERS

Paper I

Resolving Mass Spectral Overlaps in Atom Probe Tomography by Isotopic Substitutions – Case of TiSi^{15}N

David L. J. Engberg, Lars J. S. Johnson, Jens Jensen, Mattias Thuvander, and Lars Hultman

I participated in the thin film deposition and in running the atom probe. All specimen preparation, characterization, and data treatment were done by me, except for the elastic recoil detection analysis. I wrote the Paper.

Published in Ultramicroscopy 184, 2018, 51–60.

Paper II

Solid Solution and Segregation Effects in Arc-Deposited $\text{Ti}_{1-x}\text{Si}_x\text{N}$ Thin Films Resolved by ^{15}N Isotopic Substitution in Atom Probe Tomography

David L. J. Engberg, Lars J. S. Johnson, Mats Johansson-Jöesaar, Jun Lu, Magnus Odén, Mattias Thuvander, and Lars Hultman

I participated in the thin film deposition and in running the atom probe. I prepared specimens for all analyses, did the nanoindentation, and the atom probe tomography data treatment. I wrote the Paper.

Submitted for publication.

Paper III

Self-Organized Nanostructuring in $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ Thin Films Studied by Atom Probe Tomography

Lars J. S. Johnson, Naureen Ghafoor, David L. J. Engberg, Mattias Thuvander, Krystyna Stiller, Magnus Odén, and Lars Hultman

I contributed to the atom probe tomography data treatment, interpretations, and the writing of the Paper.

Published in Thin Solid Films 615, 2016, 233-238.

Paper IV

Atom Probe Tomography Field Evaporation Characteristics and Compositional Corrections of ZrB_2

David L. J. Engberg, Lina Tengdelius, Hans Högberg, Mattias Thuvander, and Lars Hultman

I initiated and planned the study, prepared atom probe specimens and participated in the running of the atom probe. I analyzed the atom probe tomography data, measured the resistivity, and wrote the Paper.

Accepted by Materials Characterization.

Paper V

Strategy for Simultaneously Increasing Both Hardness and Toughness in ZrB_2 -rich $\text{Zr}_{1-x}\text{Ta}_x\text{B}_y$ Thin Films

Babak Bakhit, David L. J. Engberg, Jun Lu, Johanna Rosen, Hans Högberg, Lars Hultman, Ivan Petrov, Joseph E. Greene, and Grzegorz Greczynski

I planned the atom probe tomography part of the study. I prepared the atom probe specimens, participated in running the atom probe, and did the related data treatment and analysis. I participated in writing the Paper.

Published in Journal of Vacuum Science & Technology A 37, 2019, 031506.

Paper VI

Observations of Atomic Density Artefacts in Atom Probe Tomography from Microchannel Plate Multifiber Boundaries

David L. J. Engberg, Hans-Olof Andréén, Mattias Thuvander, and Lars Hultman

All ceramic atom probe specimens were made and analyzed by me, and I participated in running these specimens in the atom probe as well. I planned and wrote the Paper.

In manuscript.

ACRONYMS

APT	Atom probe tomography	Analytical
CVD	Chemical vapor deposition	Deposition
DC	Direct current	Deposition
DCMS	Direct current magnetron sputtering	Deposition
DLD	Delay-line detector	APT component
EDS or EDX	Energy-dispersive X-ray spectrometry	Analytical
EELS	Electron energy-loss spectrometry	Analytical
ERDA	Elastic recoil detection analysis	Analytical
ToF-E ERDA	Time-of-flight energy ERDA	Analytical
fcc	face-centered cubic	Material
FDA	Frequency distribution analysis	Data treatment
FIB	Focused ion beam	Specimen prep.
GIF	Gatan imaging filter	Analytical
HiPIMS	High-power impulse magnetron sputtering	Deposition
LEAP	Local electrode atom probe	Analytical
MCP	Microchannel plate	APT component
PCBN	Polycrystalline cubic boron nitride	Material
PVD	Physical vapor deposition	Deposition
RDF	Radial distribution function	Data treatment
SAED	Selected area electron diffraction	Analytical
SEM	Scanning electron microscopy	Analytical
TEM	Transmission electron microscopy	Analytical
STEM	Scanning TEM	Analytical
HAADF-STEM	High-angle annular dark-field STEM	Analytical
SDM	Spatial distribution map	Data treatment
SZM	Structure Zone Model	Deposition
WC-Co	Cemented tungsten carbide	Material
XPS	X-ray photoelectron spectroscopy	Analytical
XRD	X-ray diffractometry	Analytical
XEDS	See EDS or EDX	Analytical

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1. INTRODUCTION

Thin films are crucial for today's technical development and miniaturization. They keep pancakes from sticking in a modern frying pan, reduce reflections in glasses, and are necessary for constructing the device that lets you read this thesis (even if you are reading a printed copy).

This thesis focuses on the analysis of ceramic nitride and boride thin films with proven or potential uses in industrial metal cutting of, e.g., steels, titanium, and high-entropy alloys. Such tools must be both hard and tough to survive in the harsh environments of metal cutting for an extended period of time. However, a combination of high hardness and toughness is not commonly found in a single material, as hardness and brittleness go together, while toughness is associated with ductility. Nevertheless, by depositing a strong work piece material with a thin, hard coating, it is possible to combine these properties and significantly increase the lifetime or work temperature of the coated tool.

In order to increase the performance of the any thin film application, it is necessary to understand how growth conditions and substrates influence the resulting structure of the film, and how the structure, in turn, relates to film properties. Significant efforts in thin film analysis are required to answers such questions, some of which have resulted in this thesis.

The films studied here have been investigated using several complementary techniques, in particular a novel analytical technique called atom probe tomography (APT) that quite recently was adapted to analyzing thin films and ceramic materials [1]. While this has rendered analyses possible, it is still encumbered by artefacts that affect the spatial resolution and compositional certainty. This thesis, with included papers, is built upon material specific results that, in several cases, are attained after method development and optimization to circumvent artefacts through smoothening, averaging, compensation, or even isotopic alterations of the films themselves.

1.1 Aim

The aim of this thesis is to investigate growth-structure-property relations in hard nitride and boride thin films, as well as to show both sides of APT applied to ceramic materials; the unique capability of the technique to reveal the 3-D distribution of elements with sub-nanometer resolution versus the artefacts related to atomic positions, density, and composition commonly seen when applying APT to these materials.

1.2 Outline

The thesis begins with a description of selected substrates and hard ceramic thin films with focus on properties relevant to the conducted studies, after which thin film growth is covered in a separate chapter. The analytical techniques used to investigate the films are briefly described in Chapter 4, while Chapters 5 and 6 are devoted to atom probe tomography, as well as reconstructions and related data treatment methods. The last two chapters highlight the main results and future outlook, respectively. Finally, the papers that this thesis is based upon are included.

2. MATERIALS

Several materials systems are part of, or relevant to, the investigations presented in this work. These materials systems are presented here.

2.1 Bulk Materials and Substrates

Thin films require substrates to be grown upon, and the choice of substrate in research can have significant effects on the characteristics of the film itself, as well as influence the characterization techniques to be used. For basic research studies, single-crystal substrates may be required to explore inherent material properties, while in applied research, the substrate material is often determined by what properties are necessary for the application, e.g., in cutting tool applications, the bulk material must meet a number of demands unrelated to the film growth; strength, hardness, and thermal stability being some of the most important ones. Thus, a range of substrates were required for meeting the different demands in the studies of this thesis.

Common bulk materials for cutting tools are cemented carbides [2] and polycrystalline cubic boron nitride (PCBN) [3]. As commercial cutting tools with TiSiN coatings often consist of cemented tungsten carbide (WC-Co), it was chosen as the substrate in Papers I and II, so as to replicate the growth conditions of such commercial coatings. This composite material consists of small grains of WC surrounded by a binder phase consisting mostly of Co, but often includes small amounts of other metals. Its structure is quite similar to a brick wall, where WC plays the role of bricks while Co, which has good wetting properties [4], is the mortar keeping the bricks together. The WC grains are randomly oriented, rather than positioned in the orderly fashion of bricks in a wall. The grains are very hard and brittle, while the binder phase provides toughness, which allows the tools to be deformed without immediate brittle failure. In addition to good wetting properties, Co makes the substrates magnetic, which allows simple sample mounting using magnets, but can create drift problems during specimen preparation with focused ion beam (FIB) unless first demagnetized.

Substrates can also be chosen in order to promote epitaxial film growth, where the crystallographic structure of the substrate is reflected in the film. Since crystallographic parameters depend on the direction, the orientation of the substrate is important and different orientations can result in completely different film structure. Such epitaxial relationships between substrates and films are present in three papers of this thesis. (001)-oriented MgO substrates were used in Paper III to promote nanolabyrinthine growth of $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ and in $\text{Hf}_{0.52}\text{Al}_{0.48}\text{N}$ included in Paper VI to promote single-crystal growth [5], while (0001)-oriented sapphire (Al_2O_3) was the template for the epitaxial columns of $\text{ZrB}_{2.0}$ in Paper IV.

In Paper V, the films for the APT analyses were grown on Si(001), mainly due to low cost and ease of use. However, Al_2O_3 substrates were used for the films investigated with nanoindentation, because the relatively soft Si would have a detrimental effect on the hardness and toughness measurements. A Ta buffer layer ~ 3 nm thick was deposited on the substrates prior to film deposition so as to reduce the influence of the substrates on the structure of the films.

2.2 TiN

TiN was first used as a decorative coating in the making of jewelry, because it has a golden yellow color. It was later adopted as a protective coating and is still popular due to its versatility. However, more recently engineered materials systems like TiAlN, TiCN, and TiSiN have surpassed its cutting performance when processing selected groups of materials, or in certain modes of operation.

Pure TiN layers were used in this work as diffusion barriers between the substrate and the TiSiN films of Papers I and II. Because it is so heavily studied, it is also useful as a reference for other transition metal nitride thin films. TiN coatings for cutting tools are often grown by cathodic arc deposition. These coatings are generally dense and polycrystalline, with large columnar grains [6]. The crystals are fcc with the NaCl-type structure ($\text{Fm}\bar{3}\text{m}$ space group). The lattice parameter is ~ 0.424 nm, with each unit cell containing 8 atoms, as shown in Fig. 2.1. While bonding in ceramics most often is of ionic and/or covalent character, the color and shine of TiN reveal the metallic characteristics of the bonds.

Fig. 2.1. The NaCl-type crystal structure unit cell of TiN, with black Ti and white N atoms.

2.2.1 Alloying TiN

TiN tends to oxidize at temperatures above 500°C , which puts an upper limit to the cutting speed. In an attempt to increase the maximum work temperature of TiN by improving its oxidation resistance, oxide forming elements such as Al and Si were added to the mixture [7]. The hypothesis was that when the coatings were

exposed to air, a thin layer of SiO_2 or Al_2O_3 would be formed on the surface. As the diffusion coefficient of oxygen in oxides is much lower than in TiN, atmospheric oxygen would effectively be prevented from diffusing deeper into the material, which would otherwise occur at high temperatures and be detrimental to the lifetime of the coating.

Even though a protective layer of SiO_2 [8] or Al_2O_3 [9] can be formed, and the oxidation resistance was increased, it was not the only improvement gained from combining TiN with Al or Si. Both Al and Si are grain refining in TiN, which results in higher hardness in accordance with the Hall-Petch relation [10–12]. In addition, both AlN and SiN are immiscible with TiN over a wide range of compositions [13,14], meaning that if supplied with enough energy, phase separation into TiN and AlN or SiN will occur, which proved very useful for creating structures with good wear resistance during metal cutting. With increased alloying, the metallic bond characteristics of TiN is reduced in favor of ionic and/or covalent bonds.

While not studied in this thesis, TiAlN is a very important materials system for wear-resistant coatings on cutting tools and thereby deserves mentioning. When grown in the kinetically limited conditions of physical vapor deposition, the resulting film is a metastable cubic solid solution. When exposed to high temperatures, e.g., from annealing or friction from metal cutting, the c-TiAlN phase separates into c-TiN and c-AlN in a process called spinodal decomposition [15], which results in small coherent domains and an increase in hardness. The size of the compositional modulations found in TiAlN are of the same order as those posed for challenge here on 3-D APT characterization of ZrAlN and TiSi¹⁵N. The age hardening in TiAlN persists up to ~1100 °C, after which the c-AlN transforms into w-AlN, with loss of both coherency and hardness. Significant research and development efforts have been made in order to postpone the AlN phase transformation, including several 3-D APT studies of TiAlN [16–22].

2.3 TiSiN

Incorporating a modest amount of Si (~2.5 at. % Si [23,24]) into TiN significantly changes the structure of the coatings, decreasing the grain size while retaining the NaCl-type crystal structure of TiN. As discussed in Paper II, small amounts of Si substitute Ti in the metal/metalloid sub-lattice, however without any significant change in the lattice parameter. It was found that these coatings excel at dry cutting and high temperatures.

Nanocomposite TiSiN is a structure with phases at, or close to, thermodynamic equilibrium, as opposed to the cathodic arc deposited coatings with metastable phases studied in Papers I and II. More energy is supplied to the coatings during growth, in order to drive phase separation to the very limit, where the TiN and TiSi grains are very pure and surrounded by a Si_3N_4 tissue phase [13]. The SiN is grain refining also in the nanocomposite coatings, and the hardness reaches a maximum when the amount of Si in the coating corresponds to a monolayer

around all TiN and TiSi grains; the exact amount is thus dependent on the grain size [25]. A thin cubic SiN tissue phase [26,27] can be formed during annealing of metastable arc-deposited TiSiN, which reduces diffusion of Ti and N, thereby delaying recrystallization and significantly increasing the thermal stability [24].

The micro- and nanostructured TiSiN films investigated in Paper I and II are grown at low temperatures to allow formation of metastable phases, and not necessarily form nanocomposites with a Si₃N₄ matrix. The materials system was chosen because it is interesting from both scientific and commercial points of view. Details regarding the nanostructure needed to be determined in order to understand and model the growth in detail. This, in turn, may lead to better control of film properties, such as hardness and wear resistance.

APT was identified as a good technique for investigating the nanostructure of TiSiN, had it not been for the mass spectral overlaps of Si and N, making them indistinguishable by the time-of-flight mass spectrometry used to identify ions by the technique. By growing the films using ¹⁵N instead of ^{nat}N, the mass spectral overlap was largely avoided, as is thoroughly described in Paper I, which enabled a detailed APT investigation of the film in Paper II.

2.4 ZrAlN

ZrAlN and TiAlN are closely related, since Ti and Zr are both found in Group 4 of the periodic table. However, Zr has both the largest atomic radius and positive enthalpy of mixing of the transition metal aluminum nitrides [14,28], which results in difficulties of preparing c-Zr_{1-x}Al_xN solid solutions with $x = \sim 0.4$ or more [29,30]. In addition, the driving force for phase separation into cubic pseudo-binary nitrides is much lower than in TiAlN, while the driving force for separation into c-ZrN and w-AlN is higher than that of c-TiN and w-AlN [28].

The films investigated in Paper III are fairly close to the solubility limit, with $x = 0.31$, and grown under conditions optimized for ZrN epitaxy on MgO. This resulted in growth of a two-phase system with alternating lamellae of either c-ZrN or w-AlN, with local epitaxy of ZrN to the MgO substrates.

2.5 HfAlN

One step further down in Group 4 we find Hf, with electron configuration [Xe] 4f¹⁴ 5d² 6s². Generally, atomic radii increase when going down a Group in the periodic system. However, due to poor shielding of the nucleus by the 4f electrons, the 6s electrons are drawn toward the nucleus and the atomic radius becomes slightly smaller than that of Zr. While the density becomes significantly higher, the chemistry of Hf is very similar to that of Zr, which is why neither are found without the other, and separating them is demanding [31].

Because of the similarity of Zr and Hf, their aluminum nitrides are also similar in terms of miscibility and driving force for separation. However, by applying high fluxes of low energy ion bombardment during reactive magnetron co-sputtering,

the solubility limits of single-crystal films can be extended and it is possible to grow single-crystal $c\text{-Hf}_{1-x}\text{Al}_x\text{N}$ films up to $x \leq 0.5$ [5]. The $\text{Hf}_{0.52}\text{Al}_{0.48}\text{N}$ single-crystal films included in the study of an APT artefact in Paper VI are at the onset of phase separation, with small-scale (~ 1.5 nm) fluctuations of coherent Hf-rich and Al-rich domains [5].

2.6 ZrB_2

Transition metal diborides have potential to become the next generation of wear resistant coatings for metal cutting applications. ZrB_2 is a candidate with promising properties, such as nanoindentation hardness up to $\sim 45\text{-}50$ GPa [32]. Compared to many other ceramics, its resistivity is relatively low, which enables applications such as wear-resistant electrical contacts.

Fig. 2.2. The AlB_2 -type crystal structure unit cell in a) side-view and d) along the surface normal of the borophene sheets and hexagonally close packed layers of Zr. The resulting layered structure is illustrated in b) side-view and c) along the c -direction.

While Zr-Zr- and Zr-B-bonds are strong and ionic/covalent in character, the B-B-bonds are significantly stronger whenever they can form a single sheet of hexagons [33,34], known as borophene (in analogy with graphene). This is possible for the AlB_2 -type structured materials ($P6/mmm$ space group), to which ZrB_2 belongs. The AlB_2 unit cell contains one Zr atom and two B atoms and is shown in Fig. 2.2 a) and d). The borophene sheets are separated by layers of fcc-Zr in the c -direction, as shown in Fig. 2.2 b) and c). The unit cell is primitive hexagonal with $a = b = 3.17$ Å and $c = 3.53$ Å. The c/a ratio is high in ZrB_2 because the strong B-B bonds in each borophene sheet keep the structure together along

the a -directions, while it is expanded to the maximum in the c -direction because Zr is the largest atom to form stable AlB_2 -structure, making the Zr-B separation larger than the sum of their atomic radii [33]. The size of the spheres in Fig. 2.2 show the relative size difference of Zr and B, but the separation of the spheres has been increased to reveal the structure. The size of the unit cell is thereby not to scale with the atomic radii.

ZrB_2 was chosen as a model system to investigate how to properly analyze transition metal diborides using APT, but also to investigate the grain stoichiometry and show with certainty that excess B congregate at the grain boundaries.

2.7 $ZrTaB_2$

With the successful APT analysis of ZrB_2 , applying the technique to a more complex, ternary diboride was the natural next step. The $ZrTaB_2$ films of Paper V have similar microstructure and bonding as ZrB_2 , with columnar AlB_2 -structured grains with very high aspect ratio. Due to the difference in atomic radii of Zr and Ta being $<10\%$, ZrB_2 and TaB_2 have full solid-solubility [33]. Significant amounts of Ta can thus be found in solid solution within the columnar grains. However, for high amounts of Ta, the grain boundaries shift from B-rich to metal-rich. The films with metal- and Ta-rich boundaries were found to have increased hardness and toughness compared to $ZrB_{2.4}$.

Even though the resistivity has not been measured on the $ZrTaB_2$ films, the fact that the ATP analyses could be conducted successfully in voltage mode suggests that it could be even lower than that of $ZrB_{2.0}$. The out-of-plane resistivity, which is difficult to measure in thin films, should be of most importance in voltage-pulsed APT, and this could be reduced by the incorporation of metals, rather than B, in the column boundaries.

3. THIN FILM DEPOSITION

A thin film is a layer of material, ranging from an atomic monolayer to $\sim 1\text{ }\mu\text{m}$. By tradition, techniques for making thin films are categorized into two major branches; chemical and physical vapor deposition (CVD and PVD, respectively). To be classified as a CVD process, the material must be deposited as a result of one or more chemical reactions, whereas the processes in PVD are purely physical.

Even though there are many different CVD and PVD techniques, each branch has several characteristics in common and the two branches are in many ways complementary to each other. CVD generally produce coatings of high quality, especially when complex geometries are to be coated, but is less suited for sharp edges. The deposition rate is generally slow, but this can be compensated for by designing the reactor to provide a uniform gas flow, since this allows production of very large batches. However, all elements of the coating must be available in gas phase, which often means that toxic and environmentally unfriendly gases mixtures are used. In addition, CVD coatings are generally grown at high temperatures, as many of the required chemical reactions have high activation energies.

PVD on the other hand, can combine high deposition rate with low temperature. The absence of dangerous and environmentally unfriendly gases needed in many CVD processes makes PVD safer and less problematic to work with. All in all, this effectively reduces the cost of growing films compared to most CVD processes. Furthermore, it can retain sharp edges, which is beneficial for some cutting tools, and produce films with compressive stresses that increases the hardness. Lower temperature also enables the deposition of metastable phases.

This chapter covers parts of the theory of thin film deposition that are relevant for this thesis, as well as descriptions of the deposition techniques used to produce the investigated thin films.

3.1 Phase and Structure

The phases present and their structure in as-deposited films are highly dependent on deposition parameters. Together with the thermodynamics of the concerned materials system, it is the particle flux and the energy supplied to the system, through the flux and/or heating, that determines how the films grow. The possible phases are limited by the composition of the flux, but it is the energy that determines which of the possible phases that will form and in what structure. In kinetically limited growth conditions, it is possible to grow amorphous films, given that the energy is low enough to minimize surface diffusion [35]. With slightly more energy, crystalline clusters will nucleate at many positions and their crystal structure will depend on the thermodynamically stable phase or phases at the concerned composition. The crystallites will grow in all directions into grains until they reach their neighbors, after which lateral growth will result in columns.

Additional energy increases adatom diffusivity, resulting in fewer, but larger, grains. Even more energy may result in recrystallization during growth and the columnar structure is then transformed into an equiaxed structure. The formation of structure in polycrystalline films is summarized in general terms in the structure zone model (SZM).

3.1.1 The Structure Zone Model

The SZM reduces many practical parameters of film deposition to a few parameters directly linked to the growth process. All versions of the SZM include the growth temperature on one axis [36,37]; often normalized by the melting temperature of the deposited film (homologous temperature), but more recently also compensated for the potential energy of the arriving particles [38]. The other axis has changed during the years from substrate bias [36] and pressure [37] to the kinetic energy of the arriving particles [38].

As TiN growth with cathodic arc deposition is one example where the SZM can be successfully applied, it serves as a good starting point for describing how the growth is altered by the addition of Si in Papers I and II. The SZM by Thornton [37] in Fig. 3.1 shows how the grain size and shape develop for different temperatures and pressures. In zone 1, the adatom mobility is low, which increases nucleation and results in small grains. With increasing energy, surface diffusion start to play a more important role, while grain boundary diffusion is still limited, resulting in the competitive growth that is characteristic to zone T [39]. With even more energy the grains grow into columns that often extend throughout the entire coating, which characterizes zone 2. In zone 3, the atom mobility is high enough to allow bulk diffusion and recrystallization, resulting in a dense, large grained structure.

Fig. 3.1. The SZM by Thornton [37], reprinted with permission from [40].

TiN films for cutting applications are generally deposited in the transition zone (zone T). Barna and Adamik [39] extended the SZM by also taking impurities or co-deposited additives into account, which at least partly can be used to describe how the addition of Si affects the growth of TiN. The impurities may either be dissolved in the lattice or segregate to the surface and possibly disrupt structure forming phenomenon, reducing the grain size. The low solubility of SiN in TiN [13] is believed to be the reason behind the grain refining effect of Si in TiSiN. This is discussed in more detail in Paper II.

Although not readily described by the SZMs, the self-organized structure in Paper III fits best into zone 2, as does the depositions of the films in Paper IV, which are conducted at fairly high temperatures. For the deposition method used in Paper V, the latest version of the SZM by Anders [38], which explicitly includes plasma-based deposition and ion etching, is a better description since the Ta pulses are synchronized with the bias for energetic ion bombardment. The axes include net film thickness t^* , kinetic energy of the arriving particles E^* , and generalized temperature T^* . The thickness is reduced due to densification with increasing T^* and E^* , and can even be negative due to ion etching at high E^* .

Fig. 3.2. The SZM as adapted by Anders. Reprinted from [38] with permission from Elsevier.

3.2 Texture

Texture is the distribution of crystalline orientations in a material and can influence the properties of a material. Depending on the choice of deposition parameters, the texture may differ greatly. Amorphous materials can be

considered devoid of texture, while single-crystals are the very extreme of texturing. Polycrystalline materials have grains separated by boundaries, but can also be devoid of texture if the crystallographic orientations of the grains are completely random. However, if there is a preferred orientation or growth direction, the films will be textured, as is the case in most films studied in this thesis, although their textures differ greatly.

The TiSiN films in Papers I and II change texture from dense columnar and coarse grained, to a very fine-grained structure, that is still columnar, but with sub-structures in the nanometer scale within the columns, with the addition of sufficient amounts of Si. $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ in Paper III consists of alternating lamellae of c-ZrN and w-AlN, with the texture determined by epitaxy. The $\text{ZrB}_{2.0}$ film studied in Paper IV exhibits biaxial texture, which in this case corresponds to columnar grains with the same out-of-plane orientation and one out of twelve in-plane orientations, while $\text{ZrB}_{2.5}$, on the other hand, is expected to have random in-plane orientation. This is in contrast to the random grain orientation of $\text{ZrB}_{2.4}$ in Paper V, which was grown at a lower temperature. The other films of Paper V show fiber texture, with preferred 0001 orientation increasing with Ta content.

3.3 Epitaxy

The word epitaxy stems from the Greek words *epi* and *taxis*, which translate to “above” and “in an ordered manner”. In materials science, it refers to deposition of a crystalline phase on top of a crystalline substrate, where the structure of the film is determined by the structure of the substrate, although not necessarily the same structure. Epitaxy can be divided into homoepitaxy and heteroepitaxy. The former is simply a material deposited upon itself, with the same structure. It can be used to improve the crystal quality, or to control impurities and doping close to the surface. In heteroepitaxy, a material that is different from the substrate material is used to provide additional properties that the substrate lack, e.g., increased hardness and wear resistance, reflectivity, or corrosion resistance.

For epitaxy to occur, there must be a relation between the dimensions of the unit cells in the substrate and film. They must either be approximately the same, or have a coincidental (or magic) mismatch, where a number of unit cells in the film have approximately the same length as another number of unit cells in the substrate. If the lattice dimensions of the substrate are smaller than those of the film, the first layers of the film will be compressed in-plane to fit with the substrate, while the lattice dimensions are extended in-plane in the opposite case, resulting in either compressive or tensile stress. If the lattice dimension difference between substrate and film is too large, typically $\sim 9\%$ or more, the film will relax through the creation of misfit dislocations. Homo- and heteroepitaxy, as well as a misfit dislocation, are illustrated in Fig. 3.3.

Fig. 3.3. Schematic illustration of homoepitaxy, heteroepitaxy through strained lattice and magic mismatch, as well as misfit dislocations.

The thermal expansion coefficients of the film and substrate should be similar, otherwise the lattices will expand differently and epitaxy will either not occur because the lattice dimension difference is too large, or dislocations will be created as the lattices shrink differently after epitaxial growth at extended temperatures.

Epitaxy was instrumental in the growth of some of the films in this thesis. The self-organized structure with interleaved lamellae of the $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ thin films in Paper III appear when the conditions are optimized for cube-on-cube epitaxial growth of ZrN on $\text{MgO}(001)$, i.e., $(001)_{\text{ZrN}} \parallel (001)_{\text{MgO}}$ and $[100]_{\text{ZrN}} \parallel [100]_{\text{MgO}}$, with a nominal in-plane lattice mismatch of 8.7%. [41]. The resulting local crystallographic orientational relationships between the w-AlN and c-ZrN are $(0001)_{\text{AlN}} \parallel (001)_{\text{ZrN}}$ and $\langle 2\bar{1}\bar{1}0 \rangle_{\text{AlN}} \parallel \langle 110 \rangle_{\text{ZrN}}$. The textures in the ZrB_2 columns in Paper IV are also a result of epitaxy with the Al_2O_3 substrate. The out-of-plane relationship is $(0001)_{\text{ZrB}_2} \parallel (0001)_{\text{Al}_2\text{O}_3}$ in both $\text{ZrB}_{2.0}$ and $\text{ZrB}_{2.5}$, while the in-plane epitaxial relationships in $\text{ZrB}_{2.0}$ are realized by two different magic mismatches. The columns either exhibit $\langle 1010 \rangle_{\text{ZrB}_2} \parallel \langle 1010 \rangle_{\text{Al}_2\text{O}_3}$ alignment from a 3:2 coincidence mismatch of 0.11% between the Zr and Al lattices or $\langle 11\bar{2}0 \rangle_{\text{ZrB}_2} \parallel \langle 10\bar{1}0 \rangle_{\text{Al}_2\text{O}_3}$ alignment from a 7:8 coincidence mismatch of 0.84% between the Zr and O lattices [32,42]. The columns in $\text{ZrB}_{2.0}$ can thus have 12 different in-plane orientations (multiples of 30° angular difference), while random in-plane orientations are expected for $\text{ZrB}_{2.5}$. Lastly, the single-crystal $\text{Hf}_{0.52}\text{Al}_{0.48}\text{N}$ shown in Paper VI is grown with cube-on-cube epitaxy on $\text{MgO}(001)$, i.e., $(001)_{\text{HfAlN}} \parallel (001)_{\text{MgO}}$ and $[100]_{\text{HfAlN}} \parallel [100]_{\text{MgO}}$, with $\sim 5.7\%$ lattice mismatch to $\text{Hf}_{0.52}\text{Al}_{0.48}\text{N}$ [5].

3.4 Cathodic Arc Deposition

Cathodic arc deposition uses highly energetic arc discharges to remove material from a cathode. This material is then deposited on substrates placed in front of the cathode. The technique is also known as cathodic arc evaporation, which suggests that atoms evaporate from local arc-induced melts, but in reality, a majority of the

atoms are sublimated directly into an ionized state [43]. A negative bias is applied to the substrates to attract the positive ions, which will accelerate and impact the substrate at high speeds.

Cathodic arc was chosen as deposition technique for the films in Papers I and II because it has a high degree of ionization. This enables good control of the speed of impinging ions by the bias voltage. At high speeds, the intermixing between the substrate and the coating improves adhesion. At the same time, energy can be supplied to the coating without heating, which means that it is possible to tailor the structure of the growing films in accordance with the SZM without using high temperatures. This, in turn, is a prerequisite for growing the structures of interest in Papers I and II, as these consist of non-equilibrium phases. Lastly, cathodic arc deposition is the work horse of the commercial cutting tool industry, for efficiency reasons. Since the films in Papers I and II are grown in an industrial system with similar parameters as those used commercially, any findings can be directly related to commercial products and quickly be put into practice. Thus, basic research becomes more easily available and useful to the community.

Cathodic arc deposition can be operated in direct current (DC) or pulsed mode. In DC mode, all cathodes supply material continuously and the coating composition is adjusted by varying placement of the substrates, the ratio of element in compound cathodes, or both. In pulsed mode, the coating composition is mainly adjusted by varying the pulse frequency of different pure cathodes, but compound cathodes are also possible to use. Other factors such as re-sputtering of deposited material will also affect the final composition, but is not used for regulatory purposes [44]. The growth of the films in Papers I and II was conducted in a manner that mimics the commercial growth of such films, which is done in DC mode, as the growth rate is high.

3.5 Magnetron Sputtering

Magnetron sputtering is a very versatile set of techniques, able to grow many different phases and structures, both in lab scale and industrially. The basic principles behind magnetron sputtering revolves around a plasma. Plasma is a state of matter, like solid, liquid, or gas states. It is a quasi-neutral gas consisting of both charged and neutral particles, which have a collective behavior [45]. In sputtering processes, inert gases, often Ar, are used. The ions of the plasma are accelerated toward targets consisting of the materials to be deposited by a negative bias. Collisions with the plasma ions knock out atoms of the target, and these are then deposited onto a substrate. An equilibrium plasma, where the particles have the same temperature, can be generated by heating the gas until electrons are ionized, but the plasma used in sputtering is in non-equilibrium, where powered electrodes energize the electrons of the plasma. It is created and maintained by collisions with other Ar^+ -ions and secondary electrons. A relatively high Ar pressure is necessary for sputtering to occur, but this is unfavorable

because the collisions with Ar may scatter the ejected target material, preventing it from reaching the substrate. By attracting the secondary electrons toward the target using magnets, the degree of ionization close to the target can be sufficient for sputtering at lower Ar pressures, which is beneficial for the growth rate.

While cathodic arc deposition produces significant amounts of highly ionized atoms from the cathode material, the collisions in magnetron sputtering yield more neutrals and target ions with low charge states. This can be increased, to some degree, by applying higher power density to the target, but comes with the risk of overheating it [46]. The deposition rate is not as high as in cathodic arc deposition, but macroparticles are generally not an issue in magnetron sputtering.

The composition of magnetron sputtered films can be controlled in different ways. In case of pulsed magnetron sputtering, with several cathodes subjected to pulses of the same power, the number of pulses each cathode is subjected to is used to control the composition. In direct current magnetron sputtering (DCMS), several ways of controlling the composition are common. Co-sputtering is one option, where more than one target is sputtered simultaneously and the power applied to each target is used to tune the film composition. However, depending on the geometry of the sputtering chamber, the composition may vary at different substrate positions. The compositional differences with position are generally less significant when using a single compound target, rather than several elemental targets, but multiple targets are then required for growing different compositions.

Co-sputtering with two elemental targets was used for growing the ZrAlN films investigated in Paper III and HfAlN used in Paper VI, while the films in Papers IV and V were grown from a compound ZrB₂ target.

3.5.1 High-Power Impulse Magnetron Sputtering

The degree of ionization of the ejected target material in magnetron sputtering can be increased with higher power applied to the target. However, the power needed is too high for continuous operation, or the targets would melt. This can instead be accomplished by applying short (μ s), high-power (kW) pulses with a low duty cycle. This technique is known as high-power impulse magnetron sputtering (HiPIMS) and allows more flexibility and control of the film growth than DCMS, but requires specialized equipment, in particular the power sources.

A hybrid HiPIMS/DCMS technique [47–49], where several targets are controlled individually in either pulsed or continuous deposition mode was used in Paper V to control both the metal/B and Ta/Zr ratios in the film. By synchronizing the sample bias with the time window of the pulsed Ta deposition, the energy, and thereby mobility, of the Ta ions could be adjusted. This was done during DCMS with a compound ZrB₂ target. By also varying the average power applied to the elemental Ta target, the Ta and metal fractions could be tuned. The frequency was adjusted accordingly, to maintain a constant energy per Ta pulse.

3.6 Sample Rotation

PVD techniques are line of sight techniques, meaning that material from the cathode or target will be deposited more or less in front of the source. A common way to achieve homogeneous coverage is to mount the samples on a rotating stage. In its simplest form, a 1-fold rotation, the substrates are placed on a rotating drum. By, e.g., rotating several rotating drums in the chamber, 2-fold rotation is achieved, while 3-fold rotation generally uses rotating substrate fixtures instead of drums. Each additional rotation increases the coating quality and enables more complex shapes to be homogeneously covered, but at the cost of lower deposition rates.

As cathodic arc deposition is a line of sight technique and homogenous coverage is preferred in most cases, protective coatings are in general deposited using rotation around one or more axes. However, in Papers I and II, stationary deposition was chosen because of a limited supply of ^{15}N combined with an interest primarily in the nanostructure, which should not be affected by inhomogeneous thickness. However, as the films in Papers I and II were grown without substrate rotation, they lack the compositional layering common in such films grown with single rotation. It has been shown that the sputtering yield during deposition varies with the angle of the incident ions to the surface normal [44]. Least Si is sputtered away from the film at normal incidence and it increases with the angle of incidence. This means that less Si should be sputtered away with the stationary setup compared to rotating. Thereby, a slightly higher Si:Ti ratio than what previously has been reported could possibly be achieved.

The $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ films of Paper III were, on the other hand, grown using substrate rotation [50], while the deposition of the diborides of Papers IV and V were stationary.

3.7 Reactive Deposition

When making ceramic coatings, alternate strategies for depositing non-metallic elements might be necessary. In cathodic arc deposition, the cathodes should have high electrical conductivity to sustain the arc. Conductive targets are beneficial also in magnetron sputtering to avoid charge build-up at the surface. As ceramics are inferior conductors, it is often not advisable to use compound cathodes or targets. Pure non-metallic sources are possible with, e.g., C and B, but since B targets are insulating, radio frequency sputtering is required, where the target bias rapidly shifts direction. However, this results in lower sputtering rates.

Reactive deposition is a common technique where one or more of the film constituents, generally the non-metallic elements, are supplied in gas phase and the compositions can be adjusted by controlling the (partial) pressure or gas flow. Metallic ions from the sources are subjected to a gas, e.g., N_2 , and a ceramic film is formed on the substrate through reactions with the gas.

Reactive cathodic arc deposition with $^{15}\text{N}_2$ was used for depositing the TiSiN films of Papers I and II. The ZrAlN films in Paper III and the HfAlN films in Paper VI were grown using N_2 reactive magnetron sputtering. However, for growing some materials systems, reactive deposition may be less suitable, e.g., if the possible gases are highly flammable, explosive, toxic, or environmentally unfriendly. Diborane gas (B_2H_6) diluted in Ar is a candidate for reactive growth of ZrB_2 , and has already been used for reactive sputtering of TiB_2 [51], but since it is both highly toxic, and explosive, significant investments in infrastructure and safety measures would be required. Moreover, the diborane gas can cause substantial target poisoning [51]. Poisoning is a common issue in reactive deposition. The gaseous phase will not only react with the ejected material, but also with the material at the surface of the sources. This generally reduces the conductivity of the sources. Poisoning results in a significant decrease of the deposition rate and increase of the source voltage needed [52,53]. Radio frequency sputtering can be used also on targets with decreased conductivity due to poisoning, but with reduced deposition rate compared to DCMS. Thus, the films in Papers IV and V were grown using compound ZrB_2 targets instead, which is a viable option due to the relatively low resistivity of ZrB_2 compared to many other ceramics.

3.8 Hardening and Strengthening Mechanisms

There are many mechanisms to increase the strength or hardness of a material. Since many of these are determined by the conditions during growth, the most important mechanisms for the concerned films will be described here.

The plasticity of a material is highly related to the movement of dislocations (slip), as well as twinning. Twins are generally formed from shear stress and consist of two mirrored lattices with a specific relationship. The formation occurs simultaneously over many atomic planes and the atomic movements are not restricted to the lattice dimensions. Dislocations are crystallographic defects that require a small amount of energy to move one step in the ordered structure of a lattice, generally along close packed planes, but are hindered by disturbances of this order until sufficient energy is supplied. This energy can, e.g., be from gentle heating (so as to avoid recrystallization and defect annihilation) or mechanical work. However, the latter also creates new defects that hardens the material and is thus known as work hardening [54]; a mechanism seldom used in processing of ceramics due to their brittleness.

Other mechanisms are focused on impeding the movement of dislocations, which can be done in several ways. By adding one or more alloying elements to a base material, dislocation movement can be impeded by the resulting imperfections of the lattice. The different sizes of the atoms in the alloy cause lattice strain, which increases the energy barrier for dislocation movement. Large alloying elements substitute the lattice atoms while small alloying elements can be located in interstitial sites. If the solubility limit is reached, precipitates of

another phase are formed and this is then called precipitation hardening or age hardening. Gentle heating, be it from deliberate annealing or friction during use, may also be needed to allow diffusion of the atoms forming the precipitates. The precipitates may prevent dislocation movement and can sometimes stop crack propagation. If the precipitates are small they may strain the lattice in order to remain coherent, which can be compared to a single solute atom straining the lattice in solid solution strengthening. Dislocations requiring more energy to go through the strained regions close to coherent phase boundaries is called coherency strain hardening [15,55].

Incoherent grain boundaries serve as strong breaches of the lattice order and thus hinder dislocation movement. When the difference in shear modulus of the two phases is significant, dislocation movement across the grain boundary is impeded, which is known as a Koehler barrier [56]. By decreasing the grain size, dislocations are likely to reach grain boundaries more often, thus slowing their movement in average. This is known as the Hall-Petch relation, or grain boundary strengthening [10–12,57]. As dislocations move faster within the ordered structure of the grain than between grains, there can be a pile-up of dislocations close to grain boundaries. The pile-up makes it easier for dislocations to cross into another grain. When the grain size decreases, fewer dislocations fit in the grain and the pile-up effect will decrease. With even smaller grains, the dislocations will be pinned in the grain, which increases the strengthening effect even more. However, there is a limit to the Hall-Petch strengthening mechanism. If the grains become smaller than a critical grain size, typically 10 nm or less, they may start to move with respect to one another [58]. This phenomenon, often called the inverse Hall-Petch effect, is caused by a deformation mechanism known as grain boundary sliding and should this mechanism be active, the effects of hindering dislocation movements will no longer determine the strength of the material.

The TiSi^{15}N of Papers I and II are hard due to solid solution strengthening. With enough Si added to TiN, the grain size is significantly decreased, which causes Hall-Petch strengthening, and the films also exhibit an exceptionally high defect density [24]. The thermodynamically most favorable state of SiN is the tetrahedrally coordinated Si_3N_4 . It has, however, been shown that thin layers of SiN can be stabilized into a cubic-related phase by cubic TiN with coherent interfaces [26,27,59]. Such coherent interfaces would cause coherency strain due to the difference in the size of the unit cell of c-TiN and c-SiN. The coherency will slow dislocation movement, but when the layer becomes too thick, the coherency is lost. Even though the grain size of the films analyzed in this Papers I and II in some cases are very small, there will be a resistance against grain boundary sliding, since energy must first be used for breaking the coherency, effectively decreasing the critical grain size [60]. In addition to this, the shear modulus of TiN and SiN differ significantly, thereby adding Koehler barriers to the list of possible mechanisms influencing the properties of TiSi^{15}N .

The self-organized nanostructure of the $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ films in Paper III are hard due to Hall-Petch strengthening and coherency strain hardening, as the thickness of the semi-coherent lamellae is only a few nanometers. However, as the phase purity could not be determined in Paper III, the influence of solid solution strengthening is yet unknown.

ZrB_2 and $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ are hard due to their structure and orientation. Columnar grains with nanometer diameters prevent dislocation movement perpendicular to the column length and thus results in Hall-Petch strengthening in two dimensions, while the strong covalent bonding of the B-rich column boundaries may prevent column boundary sliding [61]. Because the columns are 0001-oriented, the borophene-sheets are perpendicular to the direction of the indentations used to measure the hardness, and they are likely able to withstand high pressures without significant plastic deformation [62].

In the case of ZrB_2 , the small amount of substitutional Al found within the ZrB_2 columns might lead to a slight increase in hardness from solid solution strengthening, while the effect of substitutional Hf is negligible due a small amount and Hf having almost the same atomic radius as Zr. In case of $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$, a significant amount of Ta is found within the Zr lattice of the columns, which leads to solid solution hardening even though the difference in atomic radii is <10 % [33].

4. CHARACTERIZATION

To understand the relation between growth parameters and film properties, it is necessary to investigate the structure of the films at each determining scale. Because no technique can provide answers to all questions, several complementary techniques have been used in the works of this thesis. In this chapter, the general concepts of all characterization techniques used in the papers of this thesis are described. Since atom probe tomography is the focus of this thesis, only the basics will be covered here, while the next two chapters are devoted to describe this technique in great detail.

4.1 X-Ray Diffraction

When electromagnetic waves encounter obstacles or openings of the same size as the wavelength, diffraction will occur. The lattice dimensions of crystalline materials can be seen as a 3-D ordered constellation of obstacles, or scattering points. As the wavelength of light in the X-ray regime of the spectrum coincides with the spacing of crystal lattices, diffraction will occur. Characteristic radiation from the Cu K_α -transition, with a wavelength of 1.54 Å, is often used. For certain angles of incidence, the scattered waves will interfere constructively, resulting in abrupt increases in intensity. Because the angle related to such intensity peaks correspond to a specific lattice dimension, the way in which the X-rays diffract can reveal important clues to the structure of the crystal. This technique is known as X-ray diffractometry (XRD) and it has been used to evaluate all films studied in this thesis.

XRD and related techniques can be conducted in a number of different ways depending on the properties of the sample and what information is sought. The most common setup, as well as that used in this thesis, is the Bragg-Brentano, also known as powder diffraction. In this setup, shown in Fig. 4.1, the X-rays irradiate the material of interest while the angle of incidence and the detector angle are scanned, but always kept equal relative to the sample. At certain grazing angles θ , as defined in Fig. 4.1, constructive interference of the X-rays reflected in the crystal planes will occur, yielding an intensity peak in the detector at 2θ angle relative to the direction of the incident X-ray beam. Because of this angular dependence, measurements conducted in the Bragg-Brentano setup is often referred to as θ - 2θ -scans.

With this setup, only planes that are close to parallel with the surface contribute to the peaks. For heavily textured samples, it is important to know how they are oriented in order to get the diffraction peaks at correct angles. Should there be an offset, this can be measured by fixing the θ - 2θ angles at a known peak and tilt the sample until the diffraction peak is found, after which the entire θ - 2θ diffractogram can be shifted the appropriate amount. However, when

investigating powders or polycrystalline non-textured coatings, there will always be some grains oriented in such a way that their planes are parallel to the surface. Since only part of the sample contributes to the peaks, the intensity is decreased compared to single-crystals, but this can be counteracted by longer measurement times or wider slits. The divergence slit in the primary optics (source) determine the angular spread of the X-ray beam, while the receiving slit in the secondary optics (detector) determine what angles are accepted by the detector and reduces noise. Wide slits allow grains with larger angular deviation from parallel to the surface to contribute to the intensity peak, but this will broaden the peaks as the angular uncertainty increases.

Because the lattice spacing varies between different crystals and in different directions of the same crystal, the angles θ at which intensity peaks occur can be used to identify the crystal structure of the sample. The different phases of the investigated materials are identified using reference diffractograms from an international database containing both measurements of high-quality samples and theoretically calculated values.

Fig. 4.1. The Bragg-Brentano, or powder diffraction, setup of the XRD system.

However, care must be taken when identifying peaks, since everything that affects the size of the lattice e.g., alloying or strain, will shift the spectrum. In addition, the peak width will vary with the average size of the diffracting regions, which is often used to estimate the grain size.

X-rays interact weakly with matter and will often penetrate deep into the material. In the case of thin films there are often significant signal from the substrate. Since the irradiated area of the sample is relatively large, typically of the order of mm^2 , average properties are attained. The irradiated area changes with θ , but since the penetration depth also changes, the irradiated volume, which influences the intensity, is approximately the same. In some cases, in particular for very thin films or when substrate and film peaks overlap, it might be necessary to use other setups than Bragg-Brentano, e.g., grazing incidence XRD, where the

grazing angle θ is fixed at a very low value to decrease the penetration depth and increase the film ratio of the probed volume, while the detector angle relative to the beam direction is varied, rather than fixed at 2θ . This was, however, not required for the ~ 400 nm or thicker films in this thesis.

4.2 Electron Microscopy

Electron microscopy is a collection of different techniques that all uses accelerated electrons to characterize a sample. Because of this, they have much in common. One important benefit of electron microscopy compared to light microscopy is the resolution limit, which states that the size of the smallest resolvable object is on the order of the wavelength used to image it. The wavelengths of light visible to the human eye is in the range of 380-740 nm, which sets the absolute resolution limit. Even though it is possible to go beyond the wavelength range of the human eye by the use of detectors, the probability of light-matter interactions decreases rapidly with wavelength.

The wavelength of electrons depends on their speed, so by accelerating electrons using a bias, their wavelength can be tuned. Even though the probability of electron-matter interactions drops with decreasing wavelength, the change is not as rapid as the decrease of light-matter interactions. Instead, the resolution of electron microscopy is limited by the poor quality of electron lenses compared to their optical counterpart, and in some cases the size of the excitation volume.

4.2.1 Excitation Volume

An accelerated electron that interacts with a sample may scatter several times before its energy is lost, or it has found its way out of the sample. Statistically, the electrons interact with the atoms of a sample in a volume shaped like a teardrop hanging where the electron beam meets the sample. This teardrop shape, shown in Fig. 4.2, is called excitation volume and its size depends on the electron energy and the material in question. The teardrop shape is, however, only found if the sample is sufficiently thick.

As the electrons interact with matter, a number of processes can occur that may generate new signals, such as secondary electrons, Auger electrons, and X-rays, which can be detected. Depending on at what depths these processes occur, different signals may, or may not, reach the detector. The width of the excitation volume is of importance for the spatial resolution in electron microscopy and related techniques. This will be discussed further for each applicable technique below.

Fig. 4.2. A cross-section of the excitation volume in electron microscopy, i.e. the volume where electron-matter interactions are most likely to occur when a sample is hit by a beam of accelerated electrons. The detectable signals from different sample depths are also shown.

4.2.2 Scanning Electron Microscopy

A focused beam of accelerated electrons scanning over the surface of a sample is the working principle of the scanning electron microscope (SEM). At each position, the secondary electrons generated by the beam are accelerated toward a detector and the number of secondary electrons determines the brightness of the related pixel on the display. The secondary electron yield varies with the acceleration voltage, as well as the work function and atomic number of the surface atoms, but the local curvature of the surface has the most significant effect. Because of this, SEM is a good technique for getting an overview of the film surface.

Secondary electrons are generated throughout the entire excitation volume, but their energies are generally low, so most of the electrons reaching the detector have been generated fairly close to the surface. The width of this region is larger than the width of the electron beam, but smaller than the width of the entire excitation volume.

In the work of this thesis, SEM was primarily used as a part of all APT specimen preparation in the FIB instrument, which also includes a beam of accelerated Ga^+ ions for both imaging and milling, as well as a gas injection system for local ion- or electron-beam-induced CVD. Moreover, one part of the compositional analysis of TiSiN in Paper I was conducted within a SEM instrument and cross-sectional SEM was used in Paper V to show large-scale differences in the structure depending on the film composition.

4.2.3 Transmission Electron Microscopy

In transmission electron microscopy (TEM), a relatively broad electron beam is detected after passing through the sample. This means that the sample must be very thin, both to allow the electrons to pass through and to produce clear micrographs. Ideally, the sample should be thin enough that an electron scatters no more than once before leaving the sample, which corresponds to nanometer thicknesses. In addition, the likelihood of overlapping features that make micrographs hard to interpret becomes larger with increasing thickness. As the electrons scatter only once, the excitation volume is reduced from its drop-shape into a disc with approximately the width of the electron beam, which increases the spatial resolution compared to SEM. The low quality of the electron lenses is instead the limiting factor of the resolution in TEM.

The microscope can be used in different ways to investigate different aspects of the sample. In its most straightforward way of operation, an image is formed in the focal plane and the contrast is generated by the difference in phase between the electrons. If an image instead is formed in the back focal plane, a 2-D diffraction pattern appears. This pattern is closely related to the 1-D diffraction pattern recorded with XRD using the Bragg-Brentano setup, as crystals can diffract accelerated electrons in the same way as X-rays.

By inserting an aperture into the back focal plane, different features of the diffraction pattern can be selected, which influences the micrograph in the focal plane. If the center spot is chosen, dark areas will correspond to diffracting grains, which is known as bright-field. If another part of the diffraction pattern is selected, the micrograph in the focal plane will only be bright in areas that contribute to that part of the diffraction pattern, which is known as dark-field. An aperture can also be used in the image plane to select a certain area. The resulting diffraction pattern is then called a selected area electron diffraction (SAED) pattern and may reveal the crystal structures in the selected area.

While a dark-field TEM micrograph with SAED pattern was used in Paper I to compare the size of the compositional fluctuations with the smallest diffracting features in $\text{Ti}_{0.81}\text{Si}_{0.19}^{15}\text{N}$, both bright- and dark-field TEM with SAED patterns were used in Paper II to show the difference in structure and texture of $\text{Ti}_{0.92}\text{Si}_{0.08}^{15}\text{N}$ and $\text{Ti}_{0.81}\text{Si}_{0.19}^{15}\text{N}$. In Paper IV, a bright-field cross-sectional micrograph shows the extension of the columnar $\text{ZrB}_{2.0}$ grains, while in Paper V, bright-field TEM micrographs are used in combination with SAED patterns to show the difference in structure and texture with increasing Ta content. In-plane bright-field TEM micrographs with SAED patterns also show the changes in column width and preferred out-of-plane growth orientation in $\text{Zr}_{1-x}\text{Ta}_x\text{B}_y$.

In Papers II, the Fourier transform of a selected part of a high-resolution TEM micrograph is used to reveal prominent spatial frequencies. The pattern shows arcs due to the bending planes, in a pattern otherwise related to cubic-phase material.

4.2.4 Scanning Transmission Electron Microscopy

Scanning TEM (STEM) uses a focused beam of accelerated electrons that is scanned across the sample while the transmitted beam in each point is used to form a raster image. The resolution of the image is thus dependent on the size of the electron beam.

High-angle annular dark-field STEM (HAADF-STEM) uses a separate detector to detect electrons that scatter incoherently from the nuclei in the sample. The scattering angle is highly dependent on the atomic number (Z), which is why the technique is sometimes referred to as Z -contrast STEM. It can clearly distinguish different phases if the constituents have large differences in Z . It was used in Paper III to show the nanolabyrinthine structure of $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$, with alternating lamellae of c -ZrN (high Z) and w -AlN (low Z), as well as the ZrN precipitates at 900 °C deposition temperature. Z -contrast STEM was also used in Papers IV and V to show the B-rich boundaries (low Z compared to ZrB_2), and in Paper V also to show that the boundaries in $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ are metal rich (Zr and Ta, high Z compared to ZrTaB_2).

In Paper IV, Fourier transform patterns of a STEM image show the $\sim 30^\circ$ difference in rotation around the c -axis between two neighboring grains, while in Paper V, energy-dispersive X-ray spectrometry (EDS, in some cases also abbreviated EDX or XEDS) was used in STEM to generate qualitative composition maps of the metal distribution in $\text{ZrB}_{2.4}$ and $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$.

4.2.5 Electron Energy-Loss Spectrometry

The energy of the transmitted electrons in TEM and STEM can be analyzed with a specific instrument called Gatan imaging filter (GIF), which measures the electron intensity as a function of their energy. The initial energy of the electrons depend on the acceleration voltage and the energy spread should be low. As the electrons pass through the sample, they may interact with electrons of the sample material and lose energy. The intensity is generally plotted as a function of the difference in energy from the maximum, i.e., the energy loss. As most electrons do not interact with the sample, the zero-loss peak is extremely intense. Electrons that interact, do so mainly through plasmonic excitations of the valence electrons (plasmon loss) or by knocking out core electrons (core loss). The probability of plasmon loss is larger than for core loss, resulting in intense plasmon loss peaks compared to core loss peaks. The energy lost to plasmonic excitations are typically 10-100 eV, while knocking out core electrons require more energy. Since knocking out a core electron require enough energy to excite it into a vacant state above the Fermi level, the peak shape will reflect the electron density of states above the Fermi level, as well as the transition probability, and be characteristic to the transitions in question.

Peaks from core loss are known as edges due to their abrupt increase in intensity. Because they are found in the tail of the more intense plasmon peaks, background subtraction is important for quantification using the intensity at

different edges, unless the sample is very thin. For optimal results, the sample should be thin enough to ensure that the electrons do not scatter more than once, as this will broaden the peaks, or even make them undetectable.

Electron energy-loss spectrometry (EELS) was used in Paper V to show the difference in the edge at ~ 188 eV energy loss of the potentially overlapping K edge of B at 188 eV and $M_{4,5}$ edge of Zr at 180.0 eV [32] between column and column boundaries of $ZrB_{2.4}$ and $Zr_{0.8}Ta_{0.2}B_{1.8}$ films with either B-rich or metal-rich boundaries.

4.3 Energy-Dispersive X-Ray Spectrometry

EDS is used in combination with SEM or STEM. It can identify what elements a region of a sample consists of by means of electron-matter interactions. Occasionally when an accelerated electron collides with an atom, part of its kinetic energy is used to remove another electron from a low orbital of the atom. The atom is then in an excited state, but will eventually return to a relaxed state as an electron from a higher orbital fills the lower. This relaxation process releases energy by emission of radiation (or of a valence electron, which is then known as an Auger electron). The energy of the radiation, typically found in the X-ray range of the wavelength spectrum, will be characteristic of the transition in question, more specifically the energy difference between the two orbitals, which in turn is element specific. By scanning the electron beam and detecting the wavelength of the emitted light, the composition of a sample can be determined. As the technique relies on electron-matter interactions, it is most suitable for detecting elements with a high atomic number, since these have more electrons and are thus more likely to interact with the electrons of the beam. Atoms with low atomic number thus produce fewer counts, which may decrease the accuracy and certainty of quantitative analyses [63], and is one reason why the N concentration measured by several techniques in Paper I differs the most.

The spatial resolution of EDS varies depending on the excitation volume. The characteristic X-rays measured interact weakly with matter, and will thus have no problem of reaching the detector, but they are only generated if the accelerated electrons have enough energy to knock out core electrons, thus excluding the edges of the drop-shaped volume. Unless the sample is very thin, such as in EDS conducted in STEM, this part of the excitation volume will be significantly wider than the electron beam, which otherwise is the limiting factor of the spatial resolution of EDS. The resolution is generally too low to provide all the details of the fine-grained as-deposited TiSiN structure, but can be used as a complementary technique to determine the average composition in a large volume, as was done using an SEM in Paper I. Qualitative STEM EDS maps showing the metal distribution in $ZrB_{2.4}$ and $Zr_{0.8}Ta_{0.2}B_{1.8}$ are included in Paper V.

4.4 Elastic Recoil Detection Analysis

In time-of-flight energy elastic recoil detection analysis (ToF-E ERDA), accelerated heavy ions, $^{127}\text{I}^{8+}$ in the case of this thesis, hit a fairly large (typically mm^2) area of the sample from a pre-defined incidence angle. The ions have enough energy to remove atoms from the sample through elastic collisions. At a specific angle, these recoiled atoms pass two timing gates and the time-of-flight between the gates of each atom is measured before they hit an energy sensitive detector. The time-of-flight relates to the mass of the recoiled atom while the energy relates to the depth from which it originated.

Plotting the energy as a function of time-of-flight (or vice versa) of all recoiled atoms produces banana-shaped curves that can be ranged to a specific element, or as was done in Paper IV, even isotopes (in case of light elements). This enables depth profiling of the sample composition to depths of the order of μm , depending on the sample material, angle of incidence, and ion energy. A window excluding the surface region (and substrate region when applicable) of the depth profile is used to attain average film composition.

Using ERDA, the average composition of the films studied in Papers I-V were determined. It was generally used as a comparison the APT composition, since the probed volume of APT is much smaller. ERDA is most often a better choice than EDS for quantitative analyses involving light elements, such as B and N, because X-ray intensity depends on Z [63], while the Z -dependence in recoil probability is significantly lower.

4.5 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) uses light with a constant wavelength in the X-ray part of the spectrum to excite electrons in the material of interest. The kinetic energy E_K of the photoelectrons is measured and related to the constant energy of the impinging photons $\hbar\omega$ using Eq. 4.1,

$$\hbar\omega = E_K + E_B + \phi. \quad (4.1)$$

where E_B is the binding energy of the electron to the nucleus in relation to the Fermi level and ϕ is the work function of the material. The different binding energies measured reflect what bonds are common in the material, from which elemental ratios can be deduced. The X-rays illuminate a region in the order of 0.1 mm^2 and penetrate deep into the sample, but since $\hbar\omega$ is often $\sim 1.5 \text{ keV}$, and E_K cannot be larger than $\hbar\omega$, the analysis is limited to the depth from which photoelectrons can escape, typically no more than a few nanometers. Measured elemental ratios are thus an average of the surface, which may differ from bulk and is also strongly affected by surface contaminations. Prior to the measurement, the surface can be sputter-etched with beams of accelerated ions to remove such

contaminations, but the sputter cleaning process itself may also influence the composition.

For accurate peak positions and chemical shift identification, the energy scale must be calibrated. This is commonly done using the C1s peak from adventitious C, although using this peak for reference in XPS gives dubious results, and should be avoided, as this carbon is not a defined compound and its peak aligns to the vacuum level of the sample [64]. Alternative calibration methods involve also taking the sample work function into account [64] or calibrating according to ISO standards [65,66]. Peak identification can be complicated further by overlapping peaks. Peak fitting is used to convolute the different contributions of such peaks. In addition, background correction must be done before elemental ratios are determined.

XPS calibrated using ISO standards was used in Paper V to acquire the bonding characteristics of ZrTaB₂. The same ZrB₂ films investigated in Paper IV have also been characterized by XPS in a separate Paper [67].

4.6 Nanoindentation

Nanoindentation is used to determine mechanical properties, such as hardness and elastic modulus, from thin films. A hard and sharp tip (often diamond) is pressed into the film with increasing load and the displacement of the tip is measured. After a holding time at maximum applied load to monitor drift, the displacement is measured as the load decreases. The data is used to generate a load-displacement curve, which is shown in Fig. 4.3.

Fig. 4.3. Load-displacement curve from nanoindentation.

Parts of the curve can then be fitted to a model, e.g., the widely used model by Oliver and Pharr [68]. The hardness H is given by Eq. 4.2,

$$H = \frac{L_{\max}}{A_r} \quad (4.2)$$

where $L_{\max}$ is the displacement at maximum load and A_r is the residual indentation area in the sample. The latter is dependent on the indenter geometry and the contact depth. An area function that describes the projected indentation area A_p as a fitting of the indenter depth h was used to estimate A_r .

The reduced Young's modulus, E_r is given by Eq. 4.3,

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A_p}} \left(\frac{dL}{dh} \right) \quad (4.3)$$

where (dL/dh) is the slope of the initial part of the unloading curve, and A_p is the projected indentation area estimated using an area function. The elastic (Young's) modulus of the sample E_s can then be found using Eq. 4.4,

$$E_s = (1 - \nu_s^2) \cdot \left(\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i} \right)^{-1} \quad (4.4)$$

where ν_s and ν_i are the Poisson's ratios of the sample and indenter, respectively, while E_i is the Young's modulus of the indenter.

As mentioned, indenters can have different geometries. A common geometry, and the kind used in Papers II and V, is the Berkovich indenter, with a three-sided pyramid shape. In Paper V, a cube-corner indenter was also used, which is similar to the Berkovich indenter, but sharper, so as to produce higher stresses and strains in the contact area. Since both the estimated values of H and E depend on A , deviations in the tip geometry from the ideal case must be accounted for in order not to affect the resulting values.

A loading-unloading curve is acquired from each indentation. Clearly deviating values from unsuccessful indentations can be excluded, after which average values of hardness and elastic modulus can be estimated based on several curves. In thin film samples, it is important that the measured mechanical properties are not influenced by the properties of the substrate. A rule of thumb is not to indent deeper than 10% of the coating thickness, and thickness of $\sim 1 \mu\text{m}$ or more is desirable.

In Paper II, the hardness of different compositions and structures of TiSi^{15}N was presented and compared to literature in order to show the insignificant effect of the stationary growth conditions and the isotopic substitution. In Paper V, both the hardness and the elastic modulus of $\text{Zr}_{1-x}\text{Ta}_x\text{B}_y$ was estimated from several nanoindentation measurements. H/E and H^3/E^2 were also presented, as they are qualitative indicators of toughness and wear resistance, respectively. The

toughness was also estimated from measurements of the average length of radial cracks around cube-corner indents [69].

4.7 Four-Point Probe

The in-plane resistivity ρ of a thin film can be derived from four-point probe measurements of the sheet resistance R_s . Low resistivity is important for certain applications, such as wear-resistant contacts, but relative changes in the same materials system is generally a good measure of crystal quality. The technique uses four equally-spaced, colinear connectors that are applied to the film at the same time. A current I is applied between the outermost probes and the voltage drop ΔV between the inner probes is measured. The sheet resistance of a thin film is then calculated using Eq. 4.5,

$$R_s = C \cdot \frac{\pi}{\ln(2)} \cdot \frac{\Delta V}{I} \quad (4.5)$$

where C is an edge effect correction factor that depends on the shape of the sample and the location of the probes relative to the center [70,71]. With known film thickness t and an insulating substrate, the in-plane resistivity of the film can be calculated using Eq. 4.6.

$$\rho = R_s \cdot t \quad (4.6)$$

Four-point probe measurements were done in Paper IV to investigate whether the electrical resistivity can be related to the thickness of the grain boundaries.

4.8 Atom Probe Tomography

The main principle of atom probe tomography is controlled destruction of the specimen. A very small volume of the film is shaped into a tip with an apex diameter of the order of 100 nm. A DC voltage is applied between the tip and a counter-electrode. The voltage is adjusted so that the atoms at the apex almost field-evaporate. By applying short voltage or thermal pulses in addition to the DC voltage, the atoms at the apex will successively be pushed over the field-evaporation threshold. The tip is kept at cryogenic temperatures in order to reduce surface diffusion on the apex and, in case of thermal pulsing, to reduce the risk of heat build-up. The DC voltage is regulated so that the evaporation rate (ions per pulse) is kept constant at fractions of a percent to decrease the probability of field-evaporating more than one atom per pulse.

The atoms are often ionized and while they are still in the vicinity of the tip, electrons may tunnel back, thereby increasing the charge state in a process called post-ionization [72,73]. The electric field between the tip and the counter-electrode accelerates the ions toward a microchannel plate (MCP), which consists

5. ATOM PROBE TOMOGRAPHY

Since APT is the focus technique of this thesis, it will be described in-depth in this chapter. The basics of APT is summarized in Section 4.8, while Chapter 6 focuses on the APT reconstruction and data treatment methods.

5.1 Specimen Preparation of Thin Films

APT requires the specimens to be sharp tips while the samples of interest are thin films. Either the films must be deposited on sharp tips, or sharp tips must be made from already deposited films. The first option is generally poor because the growth will be affected by the choice of substrate and its geometry. Thus, small pieces of films are removed using a lift-out procedure [74] in a FIB instrument. The pieces are attached to readymade truncated tips of doped Si using local electron and/or ion beam-induced CVD of, e.g., Pt or W, after which the ion beam is used to shape the pieces into tips with a diameter of about 100 nm using an annular milling pattern.

The FIB instrument combines an SEM with a beam of Ga^+ ions, or more recently Xe^+ ions. Even though electrons primarily are used for imaging, and ions primarily for milling, both beams can be used for imaging and, with the addition of locally applied gas, for depositing material.

The APT specimens in all papers of this thesis were made using a focused beam of Ga^+ -ions accelerated by 30 kV, which can result in implantation of Ga into the volume that will later be reconstructed. This problem was minimized by protecting the tip from implantation of milling ions with a cap of Pt or W. A thin capping layer was deposited using electron-induced CVD, after which a thick ($\sim 1 \mu\text{m}$) layer was deposited on top using ion-induced CVD. Pieces of film from underneath the cap were then removed from the rest of the film. What remains of the cap after annular milling was removed by milling with Ga^+ ions using a lower acceleration voltage (5 kV), effectively reducing the implantation depth [75].

5.2 The Instrument

The atom probe instrument used in the papers of this thesis, Imago local electrode atom probe (LEAP) 3000X HR, has some additional components compared to the main principle described in Section 4.8. A schematic image of the LEAP 3000X HR system is shown in Fig. 5.1. Because Paper VI regards an instrumental artefact found in this particular system, its components will be described here.

Fig. 5.1. The main components of the LEAP 3000X HR instrument. The components are not to scale.

5.2.1 Local Electrode and Pulsing

LEAP 3000X HR uses a local electrode as counter-electrode, which is beneficial since the specimens are made from thin films and local electrodes do not require wire specimens [76,77]. It is possible to do both voltage and laser pulsing with the instrument. The laser has a fixed pulse duration and wavelength of 532 nm (corresponding to green color), while the pulse energy and frequency are adjustable. Similarly, the frequency and strength of the voltage pulse can be adjusted. This strength is commonly referred to as the pulse fraction, since it is given in percent of the applied DC voltage. As the DC voltage increases, so does the pulse strength, until the voltage supply reaches its maximum, after which the pulse fraction and pulse strength gradually decrease.

5.2.2 Reflectron

The reflectron is essentially an electric field, generated by a set of negatively charged rings and a grounded mesh that the ions pass through twice. It acts as an electro-static mirror and is designed to alter the flight path of the ions in accordance with their speed [78]. Fast ions, with high kinetic energy, travel far into the reflectron before their trajectory is deflected toward the detector, while ions with low energy travel a shorter distance. As the length of the flight path is adjusted to fit the ion speed, the differences in the time-of-flight for each ion kind decreases, resulting in higher mass resolution.

The kinetic energy spread of field-evaporated ions depends on the potential the ions experience between the specimen apex and the counter-electrode. For voltage-pulsed APT, this varies depending on the shape of the applied pulse in relation to when during the pulse field evaporation occurs. However, ions created by thermal pulsing, i.e., laser-assisted APT, experience a potential that is constant throughout the flight of a single ion. Since this results in a low energy spread, the reflectron will only provide minor improvements to the mass resolution. However, in the case of comparing different models of the LEAP 3000X instrument, the reflectron fitted models also have significantly longer flight paths, 382 mm compared to 84 mm [79], which improves the mass resolution.

Occasionally, ions collide with the reflectron mesh and are lost, thereby decreasing the detection efficiency. In addition, the trajectory of ions passing close to the mesh can be slightly shifted by lensing effects. This aberration is occasionally observed as a square pattern in field evaporation images [80].

5.2.3 Microchannel Plates

Microchannel plates were first developed as amplifiers in image intensifiers [81], but in a certain mode of operation, they can also be used as position sensitive single photon or single particle detectors. It can be described as an array of holes, where each hole acts as an electron multiplier. Although square configurations exist, a hexagonal pattern of circular holes is the most common. Photons or particles that hit the channel wall of the holes create several secondary electrons. The secondary electrons are then multiplied whenever they hit the channel wall, resulting in a cascade with an exponential increase in the number of secondary electrons, up to a certain point, after which a plateau in the number of electrons is reached due to channel saturation. A voltage is applied to the MCP to direct the electrons through the channel. The length-to-diameter-ratio is an important property of the channels which, together with the applied voltage, determine the gain (output-to-input ratio). For single particle detection, the output must not scale linearly with the input, and saturation is thus not an issue. For a single straight MCP, saturation occurs at gains of 10^4 - 10^5 [82–84]. This gain is too low for many practical applications, which is why single photon or particle detectors typically employ either curved channels, or up to three straight channel MCPs in series. Straight channels have a bias angle ϵ , so as to avoid that the particles hit the channel wall too deep, since such impacts have reduced gain from decreased effective length-to-diameter-ratio. The bias angles of MCPs in a series are generally the same, but in opposite direction compared to the previous. This is known as chevron or Z-stack configuration for two and three MCPs in series, respectively. It combines the benefits of curved channels while being easier to mass produce. A single MCP channel in chevron configuration is shown in Fig. 5.2. Series of biased channels, or single curved channels, produce higher gains compared to straight channels, while also reducing the problem with ion feedback, where positive ions are created instead of electrons. Due to their charge, the ions

are accelerated toward the front of the MCP rather than the back. When the ions hit the channel wall they create new secondary electrons that spread the electron burst in time or produces afterpulses. Such afterpulses vary in strength and number for each real pulse, and there is a risk that they are interpreted as false multiple detection events in APT. Luckily, the curves or changes in angle of the channels reduce the flight length of the ions in the MCP channels, thereby minimizing the effect of ion feedback.

Fig. 5.2. Cross-section of an MCP channel in chevron configuration with bias angle ε . In APT, the MCP is operated so that ion impacts most often result in saturated bursts of electrons.

The MCP in the LEAP 3000X HR consists of two MCPs in chevron configuration, as shown in Fig. 5.2, each with a length-to-diameter-ratio of 40. The MCP is manufactured in sections, called multifibers, which are fused together during the manufacturing process. Imperfections at such boundaries can induce either increased or decreased gain. In Paper VI, an artefact related to the MCP multifiber boundaries was found, which was previously not reported for APT. It is likely that the concerned MCP have higher gain at multifiber boundaries, which locally increases the detection efficiency, resulting in streaks of higher density with a chicken-wire pattern on the detector from the shape of the multifiber boundaries.

The bias angle ε of the first MCP can also result in density artefacts in straight flight path atom probes. At a specific fixed location on the MCP, the incoming ions are almost parallel to the channels of the first MCP. The ions are thus likely to start the electron multiplication process deep into the channels, which reduces the achievable gain, and thereby the number of electron bursts above the detection threshold, decreasing the local detection efficiency. Although created in the MCP, this low-density artefact is unrelated to that investigated in Paper VI, and does not manifest in reflectron fitted instruments, such as the LEAP 3000X HR used, because the angle of incidence is always smaller than the bias angle of the MCP channels.

5.2.4 Delay-Lines

A delay-line is simply a wound conducting wire of known length connected to a timer in each end. A 1-D delay-line is shown in Fig. 5.3. When hit by a burst of

electrons, e.g., from an MCP, a current propagates in both directions to the wire ends. The difference in time between the two signals, i.e., $\Delta t_x = t_2 - t_1$ using the notations from Fig. 5.3, can then be directly related to the location on the wire where the current originated, with an accuracy greater than the distance between the wires. The delay-lines are typically wound so that the electron bursts will hit several windings, but the conduction time from one line to the next is shorter than the duration of a burst, so the resulting signal is a single wide current pulse.

Fig. 5.3. Rectangular 1-D delay-line hit by an electron burst. The difference in time for the signal to propagate to the ends of the wire is related to the location on the wire.

Single delay-lines measuring both x - and y -coordinates are preferably made in a spiral shape, whereas double delay-lines are generally meandering wires in a rectangular shape, like the 1-D delay-line in Fig. 5.3, perpendicular to each other. It is possible and beneficial to include additional delay-lines, and there are hexagonal geometries for triple delay-lines [85] commercially available. The LEAP 3000X HR uses three delay-lines, where the first two are rectangular and perpendicular to each other, while the third is also rectangular, but rotated 45° with respect to the other two, as was shown using the relative dead-zone pattern in Paper VI. The first two record the x - and y -coordinates, while the signals from the third are used to solve ambiguities due to insufficient data from the other delay-lines, e.g., due to signal loss or multiple ion detections.

5.3 Field Evaporation and Related Parameters

The field evaporation [86] is affected by the applied field and temperature, as well as the shape and materials of the specimen. For a given specimen with two phases,

different regions in the parameter space result in differences in the field evaporation.

Fig. 5.4 shows the field evaporation parameter space of a two-phase material (β and γ phases), also known as a field-temperature diagram. The lines with negative slopes represent the field evaporation thresholds of the two phases, the dots represent different parameter settings in-between pulses, i.e., DC voltage and specimen base temperature, while the arrows represent either voltage or laser (heat) pulses, where the length of the arrow show their strength.

In the first case, no field evaporation will occur as no threshold is reached. In the second case, only field evaporation of phase γ will occur during pulses while phase β is preferentially retained, and the same is true for laser pulsing in case three, while voltage pulsing will yield good results. In the fourth case, field evaporation of phase γ takes place in-between pulses, while phase β will be field evaporated during pulses only. This is known as preferential evaporation of phase γ and will shift the measurement toward more of phase β , as ions from phase two will often be uncorrelated with the pulse and then be detected as background. The fifth case describes the best parameters for APT, where both voltage and laser pulsing will yield good results. In the last case, the field-evaporation of both phases are unrelated to the pulse, which leads to very high background and potential loss of information on short length scales.

Fig. 5.4. Six scenarios in the parameter space of field evaporation. 1 – no field evaporation, 2 – preferential retention of phase β , 3 – preferential retention of phase β with laser pulsing, good conditions with voltage pulsing, 4 – preferential field evaporation of phase γ , 5 – good conditions for laser and voltage pulsing, 6 – field evaporation of both phases in-between pulses.

In this simplification, the constant field and specimen base temperature should be chosen so that the dots are located below all field evaporation thresholds in order to prevent preferential evaporation. In addition, the strength of the pulses to be used (voltage and/or heat), must be sufficient to field-evaporate all phases and

elements of the specimen material, i.e., the arrow representing the kind of pulsing to be used must be long enough to reach past all thresholds.

The materials in this thesis were studied mostly using laser pulsing (horizontal arrows in Fig. 5.4). However, the low electrical resistivity of $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ and ZrB_2 enabled the use voltage pulsing (vertical arrows in Fig. 5.4) as well, which was used for the $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ APT results shown in Paper V, while the voltage-pulsed ZrB_2 analyses related to Paper IV were relatively short due to specimen fracture.

Although finding the correct parameters may seem trivial from this simplification, the matter is complicated by the fact that the applied field induces stress [87,88], which threatens to destroy the specimen, and that the field distribution is inhomogeneous, e.g., at the terrace edges of low index poles and zone lines [89]. The former caused specimen fracture of all studied materials, while the latter likely resulted in preferential evaporation of Zr in the 0001 pole of $\text{ZrB}_{2.0}$ in Paper IV. Laser pulsing can be used to reduce the field-induced stress and has enabled APT analyzes of ceramics and insulators [90], but will also bring some negative side effects. The specimen shape may have an influence on the effects of the laser pulsing and the actual strength of the laser pulse depends on more factors than the laser energy alone, e.g., the focus and alignment of the laser. Excessive laser pulsing leads to temperature build-up, with possible artefacts such as preferential evaporation and surface migration. Field evaporation can occur as long as the specimen is hot enough, resulting in thermal tails of mass spectrum peaks that cannot be corrected by the reflectron. Moreover, thermally induced field evaporation tends to produce more molecular ions [91], as is evident when comparing the two mass spectra in Fig. 5.5, making mass spectral peak overlaps more likely. The distribution of charge states seems to differ more from theoretical Kingham curves [72] in laser mode, reducing the accuracy of evaporation field estimates that are needed as input in some reconstruction algorithms.

Occasionally, even more factors restrain the available parameter range. When investigating $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ in Paper V, the analysis parameters had to be chosen so that the overlaps of $^{90}\text{Zr}^+$ and $^{180}\text{Ta}^{2+}$ at 90 Da, as well as $^{90}\text{Zr}^{2+}$ and $^{180}\text{Ta}^{4+}$ at 45 Da were avoided. While Ta^{2-4+} and Zr^{3+} were found in the best analyzes of both voltage- and laser-mode, Zr^{2+} was only found in laser-mode, Zr^{4+} was only found in voltage mode, and no Zr^+ was found. This was one of the reasons why voltage mode was used for the data presented in Paper V. The change in the charge state distribution of Zr is a result of higher total voltage $V + V_{\text{pulse}}$.

Adjustments of the analysis parameters of TiSiN in order to avoid both the overlap of $^{14}\text{N}^+$ and $^{28}\text{Si}^{2+}$ at 14 Da and that of $^{14}\text{N}_2^+$ and $^{28}\text{Si}^+$ at 28 Da in the same way as was used for $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ is most likely impossible. Hence, isotopic substitution was used to minimize the overlaps in Papers I and II instead.

5.4 Mass Spectrum and Ranging

Charged particles in an electric field in vacuum have potential energy described by $E_p = qU$, where q is the particle charge and U is the electric potential difference (voltage). When the particle leaves the electric field, all potential energy has been converted to kinetic energy, $E_k = mv^2/2$, where m is the particle mass and v its speed, resulting in Eq. 5.1.

$$qU = \frac{mv^2}{2} \quad (5.1)$$

The average speed can be described by $v = d/t$, where d is the flight path length and t is the time-of-flight. This results in Eq. 5.2, which can be re-arranged to Eq. 5.3, where $q = ne$ has been applied to replace the particle charge with the unit-less charge state n and the elementary charge e .

$$qU = \frac{md^2}{2t^2} \quad (5.2)$$

$$t = \frac{d}{\sqrt{2Ue}} \cdot \sqrt{\frac{m}{n}} \quad (5.3)$$

Since the elementary charge, ion flight length and ideally also the DC voltage are constant during each flight, the time-of-flight will only depend on the mass and charge of the particle. The mass is often given in Dalton (Da) and the unit-less charge state is used rather than the charge in Coulomb. Knowing the mass-to-charge-state ratio is often enough to identify the different ions, especially when the main components of the sample are known. A histogram, known as the mass spectrum, of the number of ions within a mass-to-charge-state ratio (or time-of-flight) range is plotted as function of the mass-to-charge-state ratio. The histogram has peaks for each kind of ion detected. It is used when assigning mass-to-charge-state ratio ranges to specific ions, a process called ranging. Two partial mass spectra from $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ are shown in Fig. 5.5.

In those cases when different ions have similar mass-to-charge-state ratios, partial or complete mass spectral overlaps will make ranging difficult. If the overlapping ions have several isotopes, these can be used, together with knowledge of the relative isotopic abundance in the sample, to estimate the ratio of the two overlapping peaks. Another option is to deconvolute the overlapping peaks [92] to aid in the ranging. Both these methods have the disadvantage of only correcting the average composition, while the ion positions remain uncertain and are applied by chance (or not at all).

If no more than one of the overlapping peaks is significant, the damage from such erroneous ranging can often be ignored, but if that is not the case, local and global compositions may be severely affected and analyses of ion distributions

may not be reliable. To circumvent this, it may be possible to fine-tune the analytical parameters so as to avoid overlaps, as was the case in Paper V, or to change the isotope distribution of the sample using isotope-enriched base materials. The latter is thoroughly covered in Paper I for the case of TiSiN, where overlaps of $^{14}\text{N}^+$ with $^{28}\text{Si}^{2+}$ at 14 Da, and $^{14}\text{N}_2^+$ with $^{28}\text{Si}^+$ at 28 Da, prevented straightforward quantitative measurements and distribution analyses by APT.

Fig. 5.5. Difference in the mass spectra of $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ using laser and voltage pulsing. Peak families of interest are labeled.

5.4.1 Mass Resolution

The width of mass spectrum peaks is directly linked to the mass resolution. What determines the mass resolution is different depending on whether voltage or thermal pulses are causing the field evaporation. For voltage pulsing, it is highly dependent on the shape of the pulse, i.e., the applied voltage over time in each pulse, but also the field evaporation rate [93]. Even if the voltage pulses during which field evaporation occur are very short, some ions will be generated as the pulses subside. This results in a range of possible ion kinetic energies, which increase time-of-flight differences and thereby reduce the mass resolution. The reflectron described in Section 5.2.2 can compensate for this difference by adjusting the flight path length. Such time-of-flight focusing improves the mass resolution at the cost of decreased detection efficiency, as some ions collide with the reflectron grids.

For laser assisted APT, with thermal pulsing, the shape and cooling characteristics of the specimen are highly influential on the mass resolution. Since laser-assisted APT can be applied to a wider range of materials and generally provides better mass resolution [90], it has been applied to all ceramic materials studied in this thesis. The laser induced thermal pulse generates ions with negligible spread in kinetic energy, but atoms may be field evaporated as long as

the tip remains heated. The time uncertainty caused by slow cooling reduces mass resolution and cannot be corrected by energy compensating instruments.

The cooling time is related to properties of the tip as well as the heating laser. Specimens with high thermal conductivity and long electron diffusion depth seem to benefit most from small laser spots and large shank angles [94]. Local heating from a small laser spot will quickly dissipate in the rest of the tip, lowering the temperature below the field evaporation threshold [95]. The heat dissipation is even quicker with a large shank angle as heat conduction along the tip increases with the cross-sectional area. Specimens with low thermal conductivity and short electron diffusion depth will instead benefit most from a large diameter [94] and short laser wavelength [96]. In such specimens, only the surface of the tip will be heated. The core remains cold and acts as a heat sink, effectively decreasing cooling times. A wider specimen means a larger core and more efficient cooling, while a smaller wavelength reduces the thickness of the heated surface layer. However, as large shank angles inevitably lead to an increase in diameter, the effects can be hard to differentiate and generalize to other materials systems than the one examined [97,98]. The same applies to short wavelengths and small laser spots, since shorter wavelengths can be focused to even smaller spots [95]. As such, the proper parameter to change in order to increase mass resolution will depend on the material and geometry of the specific tip as well as the particular instrument used in the analysis.

Since rather poor electrical and thermal conductivity are expected in TiSiN and nanolabyrinthine ZrAlN, the laser wavelength and specimen diameter are likely the most important for improving the mass resolution. Even though the thermal conductivity of the diboride films are unknown, the relatively high electrical conductivity of ZrB₂ and ZrTaB₂ suggests that these specimens should benefit most from small laser spots and large specimen shank angles, since thermal and electrical conductivity often go hand in hand because electrons are an important carrier of thermal energy.

The laser frequency is not adjustable and the same applies to the laser spot size (assuming that it is properly focused) in the Imago LEAP® 3000X HR instrument used in Papers I-VI. Changing to another instrument with laser wavelength in the ultraviolet range would also enable smaller laser spot sizes, which potentially improves the heat distribution and the mass resolution through faster cooling.

5.5 Detection Efficiency

High detection efficiency is important for investigations of small structures, as it determines how many atoms a feature must consist of to be distinguishable from the matrix. The detection efficiency is primarily influenced by obstacles in the ion flight path, such as the reflectron and the MCP of the detector.

The MCP is shaped like a honeycomb grid with circular holes. As the walls of the honeycomb cannot be made infinitely thin, some ions are bound to miss the

active area of the MCP and remain undetected. About 60% of the MCP area is active in the instrument used in this thesis, but since it is also fitted with a reflectron, its detection efficiency is reduced to ~37%. This can be compared to the Cameca LEAP 5000 XS (without reflectron) with a detection efficiency of ~80%, which is the highest of currently available instruments.

In Papers IV and V, the detection efficiency assigned during the reconstruction was used to tune the result so that the distance between Zr lattice traces in the reconstruction was $\sim 0.353 \text{ nm} = c$. This resulted in an effective detection efficiency of 32%, rather than 37%.

A major benefit of APT is that the detection efficiency is considered uniform, i.e., not dependent on atomic number, ion charge state, etc., which means that there is no need for reference samples in quantitative compositional analyses. However, as is described in the next sections, this is not always the case for materials with non-ideal field evaporation characteristics, such as many ceramics.

5.6 Correlated Evaporation

The field evaporation behavior of a material is influenced by its bond characteristics. Ceramics in general have bonds of covalent and ionic nature. When field evaporation occurs, the bonding of the remaining atoms adjacent to the newly formed surface vacancy changes. As a result, the field evaporation of an atom or molecule from a ceramic specimen is often followed by a burst of atoms and/or molecule from the same area. This process is called correlated evaporation and will reduce the accuracy of quantitative compositional analyses [99], because the APT detector is by design less likely to detect subsequent ions that arrive too close in both space and time to the first ion [79,100].

Most reconstruction algorithms, including those used in the papers of this thesis, assumes that field evaporation occurs from a hemispherical surface. With each detected ion, the z-coordinate is increased a minute (sub-Ångström) distance, so that the z-coordinate has increased about the nearest neighbor distance (sub-nanometer) in this direction when an entire hemispherical layer has been detected. This works well with materials where field evaporation occurs evenly over the entire specimen apex, but less so when correlated evaporation produces bursts of ions originating from a small part of the apex, which is often the case for ceramics.

As ZrB_2 exhibited severe correlative evaporation behavior, its evaporation behavior was studied in Paper IV and a correction of the quantitative compositional analyses was suggested and compared to an established method. Fig. 5.6 shows APT point cloud cross-sections from a 5 nm thick slice in a region close to the pole in $\text{ZrB}_{2.0}$, where each dot represents a Zr ion. Fig. 5.6 b) shows alternating dense and sparse crescents along the analysis direction (from top to bottom) due to correlated evaporation. A burst of ions in one region of the hemispherical specimen surface produces ions unnaturally close in the z-

direction, which results in the dense crescents of the point cloud in Fig. 5.6 b). In other parts of the specimen, the z-coordinate is increased, but very few ions are detected, producing the sparse regions. Because ions at protrusions have higher evaporation probability than in depressions, such as those produced by bursts, the shape of the surface will not deviate excessively far from the hemisphere assumed in the reconstruction, making the dense and sparse crescents in cross-sectional images alternate.

Fig. 5.6. 5 nm thick cross-sectional ion maps from different angles, where each dot represents a Zr ion. The ion maps show density fluctuation in the pole region of $\text{ZrB}_{2.0}$, as well as b) typical reconstruction algorithm artefacts with alternating dense and sparse crescents from correlated evaporation, and c) lattice traces, while a) and d) show no such patterns.

Fig. 5.6 a), c), and d) show the same region as in b) viewed from different angles. When the viewpoint is changed by 10° (corresponding to rotation along the vertical axis of the image into (positive) or out of (negative) the plane of the paper), the crescents cannot be seen, but for positive rotation the lattice traces used to optimize the reconstruction parameters in Paper IV are revealed, as can be seen in Fig. 5.6 c). Similar traces close to the pole were also found and used in

Paper V. In the direction perpendicular to that shown in Fig. 5.6, the crescents from correlated evaporation and the lattice traces partially overlap. Neither lattice traces, nor crescents can be seen when the viewpoint is changed to -10° or 20° , as shown in Fig. 5.6 a) and d), respectively.

5.7 Multiple Events

Two or more ions detected in the assigned time window after a single pulse is known as a multiple event. The length of the time window depends on the flight path length of the instrument and should be equal to the time for the highest mass-to-charge-state ratio expected to reach the detector [101], although very heavy ions with low charge states are occasionally detected at low mass-to-charge-state ratios in the early stages of field-evaporation, when the acceleration voltage is so low that the slow, heavy ions are detected as fast ions in the next pulse.

Materials with correlative evaporation behavior have a high fraction of multiple detection events. Together with the detector design [85], and the method used for analyzing the detector signal [102], the field evaporation behavior of the specimen [99,103] can influence the effective detection efficiency. Because of the detector design, a region around a detection site cannot detect another ion within a short period of time from a detection event. This region is called the dead-zone or dead-space, and the period of time is called the dead-time. They are related in such a way that the dead-time decreases with distance from the detection event [79]. If more ions hit the detector within the dead-zone, only the first will be detected. With each additional ion the complexity in resolving which delay-line pulse correlates to what detector event increases significantly. To improve the detection capability for multiple events, and to be able to confirm the x - and y -coordinates, an extra delay-line [85] at 45° angle to the standard delay-lines is often used.

Multiple events can also have other sources. There is noise in MCPs generated primarily from radioactive decay of the components of the glass and the residual gases of the vacuum chamber may also hit the MCP. Occasionally, this will lead to an electron burst above the gain threshold. Should this occur shortly after a voltage or thermal pulse on the specimen, a detection will be recorded. Since such events are completely uncorrelated with the pulse, the time-of-flight and subsequent mass-to-charge-state ratio will not depend on the ion mass or charge, and will thereby only contribute to the background noise. If it occurs at the same time as a field-evaporated atom is detected, the detection will be considered a multiple event. Since these multiple events are random in character, they will not affect the compositional analysis. However, multiple events involving more than one field evaporated ion can produce more severe losses. Such effects can occur either by correlated field evaporation of more than one ion in the same pulse, when the ions are in close proximity to each other on the tip, or through mid-flight dissociation of molecular ions.

5.8 Local Magnification Effects

While the reconstruction algorithms used in the papers of this thesis assumes an equilibrium specimen shape of a hemispherical cap on a truncated cone, this is inaccurate when the analyzed specimens contain several phases with large differences in evaporation field. The field evaporation probability of the low evaporation field phase is higher and the resulting shape of the apex will reflect this. The schematic image in Fig. 5.7 shows two equilibrium surfaces in cross-section. On top is the ideal, hemispherical, equilibrium surface and below is what the equilibrium surface may look like for a fiber-textured specimen, with the length of the fibers parallel with the specimen axis, if the phases have different evaporation field, similar to the situation with the grains and boundaries of $\text{ZrB}_{2.5}$ in paper IV.

Fig. 5.7. Ideal equilibrium surface (top) and the equilibrium surface of a specimen with columnar grains and different evaporation field phases (bottom).

The actual shape of the specimen surface during field evaporation alters the trajectory of field evaporated ions, which is not accounted for in the reconstruction. Consider a precipitate in a surrounding matrix phase, as shown in Fig. 5.8. If the precipitate requires a combination of higher field and temperature to field evaporate compared to the matrix phase, it will largely persist while the matrix phase is field evaporated. Eventually, the precipitate will protrude from the otherwise hemispherical surface and because such geometries locally enhance the field, the precipitate will field evaporate.

If the precipitate has a lower evaporation field compared to the matrix phase, a flat surface, or possibly a depression, will be created instead, as the precipitate atoms have higher probability of field evaporation than matrix atoms. Ions originating from a protrusion will be spread out in the x - and y -plane, while ions originating from a depression will be focused. This is shown schematically in Fig. 5.8. In addition, to the distortion in x - and y -, the field evaporation sequence is also changed, which lowers the accuracy of the ion positions in the z -direction.

Using the assumption of a constant hemispherical tip surface in the reconstruction will cause a high field precipitate to appear larger and less dense than it actually is, while a low field precipitate will appear smaller and denser. This phenomenon is often referred to as local magnification effects.

Fig. 5.8. Local magnification in APT and its influence on the measured density and size of a precipitate (black atoms) in a single-phase matrix (white atoms) for the same experimental conditions, but with different evaporation fields required for the two phases.

Fig. 5.9. B concentration and total density maps from APT in 3 nm thick slices showing a) B-rich boundaries with low density due to local magnification in $\text{ZrB}_{2.5}$ and b) B-deficient boundaries with high density due to local (de)magnification in $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ highlighted by arrows.

Local magnification is the cause of the distortion of the Zr signal in the nanolabyrinthine $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ in Paper III. In addition, the strong density fluctuations in $\text{ZrB}_{2.5}$ in Paper IV and $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ in Paper V suggest that local magnification influences the width of the column boundaries as well as the composition close to such boundaries. This is shown for $\text{ZrB}_{2.0}$ in Fig. 5.9 a) and for $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$ in Fig. 5.9 b). In the case of $\text{ZrB}_{2.5}$ (and $\text{ZrB}_{2.0}$ to a lesser extent), the measured APT density is lower in the B-rich column boundaries than in the

grains, reflecting the strong bonds and high evaporation field of B, which yields a boundary region that is protruding compared to the rest of the specimen surface and thus is spread like the high-field precipitate in Fig. 5.8. The situation is opposite in the metal-rich boundaries of $\text{Zr}_{0.8}\text{Ta}_{0.2}\text{B}_{1.8}$, which are more easily field evaporated than the columnar grains. In analogy with Fig. 5.8, the B-deficient boundaries in Fig. 5.9 b) are focused, resulting in a locally higher density.

5.9 Grain Boundary Effects

With the exceptions of the coarse-grained $\text{Ti}_{0.08}\text{Si}_{0.92}^{15}\text{N}$ in Papers I and II, and the single-crystal HfAlN included in Paper VI, all investigated films are very fine-grained in 1-D (across $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ lamellae), 2-D (perpendicular to the fiber direction in the diborides), or 3-D (feather-like TiSiN). Their properties, including field evaporation behavior, should be highly influenced by the plentiful grain boundaries, altering the film properties significantly from those of bulk single-crystals. This grain boundary effect could make the films easier to analyze with APT without ruptures, but also cause more artefacts related to differences in evaporation field. Difficulties with finding suitable experimental parameters for different compositions of HfAlN might be connected to the lack of grain boundaries.

6. APT RECONSTRUCTION AND DATA TREATMENT

6.1 Reconstruction

After the specimen has been field evaporated and the ions have been detected, a reconstruction is made to enable visualization, measurements, and data treatment methods. The purpose of the reconstruction is two-fold; to transform the detector x - and y -coordinates into coordinates in the specimen (from mm to nm) through the magnification, and to transform the flat detector hit map into a volume point cloud by assigning each ion a depth (z -coordinate) based on the sequence in which the ions field evaporated. The total volume of the reconstruction is set by the number of detected ions, the (estimated) detection efficiency, and the volume assigned to each kind of ion. The reconstruction then serves to mold this volume into a shape that reflects the analyzed volume of the specimen.

A point-projection model is commonly used, where the ion trajectories are straight and originate from a single point on the axis of the specimen, called the projection point P, as illustrated in Fig. 6.1. The model relies on the assumption that the tip assumes an equilibrium shape of a truncated cone with a hemispherical cap. While this assumption works well with single-phase material, it is only a rough estimate when analyzing specimens containing phases with large differences in evaporation field, as the resulting non-ideal equilibrium surfaces induce local magnification effects in the reconstructions [104,105]. Reconstruction algorithms not relying on the assumption of a hemispherical cap on a truncated cone are, however, under development [106,107].

Fig. 6.1. Point-projection model commonly used in APT reconstructions, where ion flight paths of length L are projected as straight lines from a projection point P, found a distance ξR from the apex along the axis of the specimen, where R is the radius of curvature and ξ is called the image compression factor. The shank angle α , as well as the x -coordinates in the sample and at the detector, x_{detector} , are also shown.

6.1.1 The Bas *et al.* Protocol

In 1995, Bas *et al.* [108] developed a general protocol for 3-D reconstructions that is still used to this day, in which a point-projection from the detector to the specimen of each individual ion is used. With the specimen modelled as a truncated cone with a hemispherical cap, the resulting magnification M can be calculated using Eq. 6.1, given that $L \gg R$ (small-angle approximation) where L is the ion flight length, R is the specimen radius of curvature, and ξ is the image compression factor, which is considered constant during each analysis. In APT, $L \gg R$ is true, since L is on the order of 10^2 mm, while R is on the order of 10^2 nm. For small angles, ξ can be seen as the theoretical angle divided by the observed angle between two crystallographic directions (regardless of whether such directions can actually be observed or not). The value of ξ ranges from 1 (radial projection) to 2 (stereographic projection), and is often found close to the middle of this range [109].

$$M = \frac{x_{\text{detector}}}{x} \approx \frac{L}{\xi R} \quad (6.1)$$

Knowing the magnification enables back-projection of the x_{detector} - and y_{detector} -coordinates of to the x - and y -coordinates of the ion in the tip. The z -coordinate is calculated using the sequence in which the ions were field evaporated, the volume assigned to the particular ion, the detection efficiency of the instrument, as well as the x - and y -coordinates, and the radius of curvature. The radius evolution can be estimated from the evolution of the applied DC voltage, V , using Eq. 6.2, where F_e is the evaporation field and k_f is the field (reduction) factor, which accounts for the fact that the tip is not a perfect sphere as well as its electrostatic environment, e.g., distance from the apex to the substrate and the counter-electrode.

$$R = \frac{V}{k_f F_e} \quad (6.2)$$

Only the product $k_f F_e$ is needed to estimate the radius evolution and a value can be found by measuring the end radius of curvature in SEM or TEM micrographs, since the end voltage is also known. This, however, assumes that the analysis is stopped before the tip ruptures from field-induced stress [87,88].

6.1.2 Tip Profile Reconstruction

Because $k_f F_e$ may vary during the analysis, the radius evolution can instead be estimated from the tip profile measured in pre-analysis SEM micrographs. This method was used in the reconstructions of Papers I and II, because measurements of the end radius of curvature was often impossible. In case the post-analysis tip was available for SEM, control reconstructions using the measured end radius of curvature were made as well.

6.1.3 The Geiser et al. Protocol

The protocol by Geiser et al. [110] was developed in response to increasing field-of-view in APT analyses. While the Bas et al. protocol relies on the small-angle approximation, which becomes increasingly inaccurate with larger field-of-view, the protocol by Geiser et al. does not. The specimen is modelled as a hemispherical cap on a truncated cone, but the radius evolution is estimated using a fixed shank angle α , rather than estimated from the evolution of the DC voltage or the tip profile, and the shank angle is also considered when calculating the volume increment of each ion.

6.1.4 Reconstructions Using Crystallographic Features

Crystallographic features, such as poles and zone lines, can be used to validate the reconstruction parameters, since their relative angles can be calculated if the crystal structure is known [89,111,112], but only in analyzes where such features manifest. While this is uncommon in ceramics, some specimens in Papers IV and V did manifest a single low-density pole artefact. Although no other poles were found to measure the angles, the increased order of the reconstruction close to a pole enabled the detection of lattice planes at small angles to the analysis direction (z), as can be seen in Fig. 5.6 c) in Section 5.6 of this thesis. An iterative reconstruction method based on the protocol by Geiser et al. [110] was used in order to optimize reconstruction parameters to match both SEM measurements of the radius of curvature and shank angles of the tip before and after the atom probe analysis, as well as flat lattice planes at consistent distances close to the c -value from literature.

Fig. 6.2. 2-D SDMs showing the separation of Zr planes in the c -direction (z) in the pole region of $\text{ZrB}_{2.0}$, in a) and b) after optimizing the reconstruction parameters. The scale of the SDM in c) is different from a) and b) and white arrows highlight the contribution from correlated evaporation. The rainbow color scale goes from low intensity (dark blue) to high intensity (red).

The planes in the pole region were investigated using 1-D and 2-D spatial distribution maps (SDM) [113], which are similar to Fourier transforms in that they can reveal spatial frequencies, but in real space rather than reciprocal space. 2-D SDMs of Zr in the pole region of $\text{ZrB}_{2.0}$ are shown in Fig. 6.2. As treated in Paper IV, the contribution from correlated evaporation could be somewhat separated from that of the lattice planes using 2-D SDMs, and is highlighted by white arrows in Fig. 6.2 c).

6.2 Voxel Size and Delocalization

When determining the local composition within an atom probe specimen, it is often convenient to sample the data. There are two common approaches when employing sampling to APT data, either a constant number of atoms per volume, or a constant shape and size. The choice depends on what kind of analysis is to be conducted. The former is, e.g., used in the original algorithm for finding a proper block size by Hetherington and Miller [114] mentioned in Paper I and the frequency distribution analysis (FDA) used in Paper II, as the data can be directly related to the binomial distribution when organized in this way. The latter choice is common for visualizing the data. For simplicity, these volumes are in most cases cubes, or at least cuboids. As such, they can be considered the 3-D version of the 2-D pixel, and are thereby designated “voxels”, for volume pixels.

Sampling is, however, a source of artefacts. Ions very close to the border between two or more voxels will only contribute to the voxel it is located in. This can be tolerated as long as the surface-to-volume ratio of the voxel is low, but with decreasing voxel size, the ratio, and thereby also the error, grows. One solution to minimize these sampling artefacts is to allow the ions to contribute partially to several voxels. A common choice is to represent each ion with an ellipsoidal Gaussian function centered on the position of each ion. The function is normalized so that the volume integral of the entire ellipsoid returns exactly one ion. In APT data treatment, this smoothening of the ion positions is called delocalization, as the ions become spatially delocalized within an ellipsoid delimited by the cut-off lengths. The cut-off is denoted the delocalization value and approximately corresponds to 3σ in statistics.

The standard settings in the IVAS software are delocalization values of 3 times the voxel edge length in the x - and y -directions, and 1.5 times the voxel edge length in the z -direction. This is because the resolution of the APT is considered best along the analysis direction, but due to the correlated evaporation behavior common in field evaporation of ceramics, this might not be true, which motivates the use of an isotropic delocalization value.

As correlated evaporation may lead to unreasonably short interatomic distances in the z -direction and the APT data in all papers of this thesis show signs of correlated evaporation, an isotropic delocalization has been chosen instead. The voxel size and delocalization parameters influence not only the visualization

of the APT data, but also certain data treatment methods, such as iso-concentration surfaces, and thus the related proximity histogram.

6.2.1 Voxel Size for Visualization of Small-Scale Fluctuations

An important part of Paper I involves finding the most meaningful voxel size in order to visualize the data in the best way. This was then used as a tool for setting the sampling parameters in Papers I, II, IV, and V. In Paper I, a previously developed algorithm used for 1-D APT data was first tested [114]. This algorithm was based on comparing the mean difference in composition of neighboring ion sequences ΔC as a function of the sequence length, also known as the ion count. If ΔC was found to be stable over a range of ion counts, the local composition would be independent of the ion count within that range. The smallest value within that range should then be chosen to maximize the spatial resolution. However, this algorithm works only for strong compositional variations [114]. It had already been successfully applied for adaptation to 3-D voxels, although all details of this conversion were not presented [115].

The algorithm used in the papers considers the 26 voxels in a 3-by-3-by-3 cube around any non-edge voxel as adjacent. Thus, it can analyze 13 discrete directions, or any combinations thereof. For $\text{Ti}_{1-x}\text{Si}_x^{15}\text{N}$ in Papers I and II, all 13 directions were combined for $\text{Si}/(\text{Ti}+\text{Si})$, whereas for the columnar structures at small angles to the z -direction of the diborides in Papers IV and V, only the four discrete directions associated with the x - and y -directions were used for B/Zr and $\text{Ta}/(\text{Zr}+\text{Ta})$. The mean ΔC in the selected directions are calculated for all non-edge voxels. The mean of the means is then plotted as a function of the mean number of ions per voxel.

Fig. 6.3. The mean difference in B/Zr of neighboring voxels as a function of mean number of ions per voxel. The experimental curve has a plateau-like region for voxel edge lengths of ~1 nm and above.

Fig. 6.3 shows the mean difference in B/Zr of neighboring voxels for different voxel edge lengths in $\text{ZrB}_{2.5}$. The experimental curve has a somewhat plateau-like region for voxel edge lengths of ~ 1 nm or more, suggesting that this is the best sampling parameters, since longer edge lengths do not significantly affect the composition, while the spatial resolution is decreased.

As shown in Paper I, however, the 3-D version of the algorithm, where the average compositional difference of every voxel with up to 26 neighboring voxels found no range in which ΔC was close to stable for the small-scale compositional fluctuations of TiSiN . Nevertheless, the results could still be made useful if the differences were compared to the noise level for the specific voxel size. The noise level was simulated by re-arranging the mass-to-charge-state ratio of the ions while keeping the average composition and ion positions the same, before the algorithm once again was applied to the APT data voxelated with different voxel edge lengths. This is shown for $\text{ZrB}_{2.5}$ by triangles in Fig. 6.3 above and for TiSiN in Fig. 5 of Paper I. If the experimental curve would have had an obvious plateau of stable ΔC -values for different number of ions per voxel (voxel sizes) as in Fig. 6.3, the difference between the experimental curve and the randomized curve would have had a maximum at the rightmost end of the plateau, corresponding to larger voxels than the leftmost end. The difference of the experimental and randomized curves in Fig. 6.3 are shown in Fig. 6.4 A similar figure for two compositions of TiSi^{15}N is shown in Fig. 6 of Paper I.

Fig. 6.4. The difference in mean ΔC (B/Zr) between experimental and randomized values as a function of mean number of ions per voxel.

Even though the experimental curve for TiSiN had no distinct plateau, there was a maximum in the plot of the difference between the experimental and the randomized curves, just like in Fig. 6.4. For $\text{ZrB}_{2.5}$, with plateau-like regions, the best option is just before the maximum, as this would correspond to best spatial resolution without changes in composition, thus 1 nm voxels were used. However, when there is no such plateau, the voxel size corresponding to this maximum can

instead be used as the best compromise between noise and excessive averaging. For practical reasons, the same voxel size of 0.8^3 nm^3 was used for all specimens even though the maxima were found for slightly larger voxels in a few specimens. This can, however, be motivated by the fact that the best choice of voxel size in the plot showing ΔC (as a function of mean number of ions per voxel) would have been at the leftmost part of the plateau, since this increases the spatial resolution compared to the rightmost part. It is thus reasonable to choose a slightly lower value than the one indicated by the algorithm, so long as the change in mean compositional difference ($\Delta C - \Delta C_{\text{random}}$) is insignificant, i.e., the slope of the ΔC difference curve is not too steep.

It is important to note that the voxel size determined by the algorithm is valid for the specific specimen, compositional fluctuation, and delocalization parameter. If another specimen or delocalization setting is to be used, or another compositional fluctuation is to be measured, new graphs can be generated to determine whether another voxel size is now the better choice. However, in cases when two different compositional fluctuations are to be compared, it can be relevant to have the same voxel size for both, as long as the difference in most suitable voxel size is not too large.

There is room for improvement of the algorithm. By automating the process, there would be no need for pre-defining a relationship between the voxel size and the delocalization, which could provide an even better choice of sampling parameters.

6.3 Radial Distribution Function

When short-range order, such as clustering behavior and corresponding length scales, are of interest, as in Paper II, the radial distribution function (RDF) is a powerful data treatment method to use. It shows how the local composition evolves at increasing distances from a particular kind of ion.

Before the analysis is started, one or several kinds of ions are selected to be centers. In the first step, spheres around each center-ion, with radii set by the user, are defined and the relative concentration of all enclosed ions is calculated. In the next step, concentric shells are defined around each sphere with the same thickness as the sphere radius, and the relative concentration of all enclosed ions is once again calculated. In the following steps, more and more concentric shells are defined and the concentration within each is calculated. The calculated average composition can then be plotted as a function of the distance from the center-ions. Depending on the number of center-ions, the first few concentrations may have large errors from counting statistics, but the volume is quickly increasing with distance, and with it the error is reduced. Because the RDF samples the data in this way, it is not dependent on the voxel size or delocalization setting, but rather the change in radius per step.

Fig. 6.5. Schematic representation of using the RDF projected to 2-D. Relative concentrations with increasing distance from a selected ion type (grey) are measured. The probed volume increases rapidly with distance.

Fig. 6.5 shows an example of volumes defined by the RDF projected to 2-D. With the ions in each shell counted, the relative concentration of a particular kind of ion as a function of distance from the center-ions can then be plotted. Comparing curves generated in the same reconstruction with different center-ions can sometimes be difficult, since the analysis will regard different parts of the sample. This is why minor constituents generally are chosen as center-ions, e.g., Cr when investigating Cr precipitates in Fe-Cr-Al alloys [116], or Si for enrichment of SiN in TiN-rich matrix, as is the case in Paper II. There are, however, exceptions where RDFs of the matrix phase can be used, e.g., in the evaluation of spinodal decomposition in Fe-Cr by Zhou et al. [117] or for passively selecting regions where the lower limit of Si in TiSiN could be evaluated in Paper II.

It is often useful to normalize each curve with the bulk concentration of that particular ion since this makes deviations from homogeneity apparent. Bulk normalized RDFs were used in Paper II.

6.3.1 Decomposed RDF

When analyzing ceramic thin films with APT, molecular ions are often present because of the covalent nature of the bonding [118] and the use of laser pulsing [91], which is often necessary. With many different molecular ions, the RDF becomes difficult to interpret if the ions of interest are part of molecular ions. Each kind of molecular ion generates an additional curve that must be superimposed on the curves of its constituent ions to grasp the full distribution of the element of interest. This is especially true in the case of RDF curves that have been normalized using the bulk composition of that particular ion, as these must be superimposed in accordance with their bulk composition.

To make interpretation of the RDFs in Paper II straightforward, the molecular ions had to be decomposed into single atoms. The algorithm does not consider the

unlikelihood of finding several atoms at exactly the same position for all the measured ions. Instead they are simply allowed to occupy the same spatial coordinates. Potential negative effects of this would most likely only be found for very short distances from the center-ions, as the increasing volume of each shell will increase averaging.

In case of molecular center-ions with more than one of the intended single center-ion, such as Si_2N in the Si-centered decomposed RDF, it was necessary to combine more than one RDF to decompose molecular ions into single. The molecular center-ions also posed a problem when decomposed, as the “extra” ions would all contribute to the concentration in the smallest volume with the lowest number of atoms. In this case, the ions were redistributed into several bins using the nearest neighbor distribution measured in that particular APT reconstruction and their contributions were also weighted with the detection efficiency, to account for the fact that each part would have had a detection probability similar to the detection efficiency if they had evaporated as single ions.

In the case of Si center-ions, which is one of the center-ions used in Paper II, this compensation for the “extra” ions generated by decomposing molecular center-ions had no significant effect on the interpretation of the RDF, but still reduced uncertainties regarding the effect of these “extra” ions, while the RDF with the other center-ion, Ti, was primarily included to avoid misinterpretations of the somewhat unconventional use of proximity histograms for determining the lowest measured Si content in Ti-rich regions.

6.3.2 Cylindrical RDF

In Paper IV, an adaptation of the RDF was applied to the investigation of the ZrB_2 column stoichiometry. In principle, the centers were elliptical cylinders within the columns, rather than a particular kind of ion. The composition in cylindrical shells, generally 1 nm wide, at increasing distances from the centers were investigated to reveal how the average stoichiometry the ZrB_2 columns varied.

6.4 Frequency Distribution Analysis

FDA is an example of an APT data treatment method where a block size is used rather than the voxel size. This means that the volume of each block is adjusted so that it contains exactly the chosen number of ions. A small number means that the compositional uncertainty within the block is larger, as the smallest compositional step is 1 at. % with 100 ions, 2 at. % with 50 ions, and 10 at. % with 10 ions etc. On the other hand, the block volume (in combination with the density) influences the size scale of the analysis, as fluctuations much smaller than the block volumes are averaged.

By combining the FDAs with the ion density, it is possible to get an indication of what feature length scales are investigated. The approximate average ion density ρ_{ion} in TiSiN have been calculated in Eq. 6.3, where n_v is the number of

ions in the volume V and ε_D is the detection efficiency based on open detector area.

$$\rho_{ion} = \frac{n_V \cdot \varepsilon_D}{V} = \frac{8 \cdot 0.37}{0.424^3} \text{ nm}^{-3} \approx 39 \text{ nm}^{-3} \quad (6.3)$$

In the calculation, the detection efficiency of 37% comes from the instrument design, while the volume and the number of ions originate from the TiN unit cell. The experimental ion density after reconstruction was $43 \pm 2 \text{ nm}^{-3}$. As the spatial size of the blocks varies, only the average characteristic length $l_{avg.}$ of the FDA analysis can be calculated with Eq. 6.4 below, where V_{avg} is the average characteristic volume of the FDA with the block size n_{block} .

$$l_{avg.} = \sqrt[3]{V_{avg}} = \sqrt[3]{\frac{n_{block}}{\rho_{ion}}} \quad (6.4)$$

With $n_{block} = 100$ ions, the average characteristic length is $\sim 1.33 \text{ nm}$ while $n_{block} = 50$ ions reduces it to $\sim 1.05 \text{ nm}$. Features smaller than this length will have limited influence on the results of the FDA, as they are averaged.

Using a fixed number of ions instead of a fixed volume is beneficial when comparing the experimentally measured concentration distribution with the expected distribution of a random solid solution of the same average composition. The random solid solution is created by re-distributing the mass-to-charge-state ratio of the ions in the same way as previously described in Section 6.2.1 for the determination of the most useful voxel size for visualization, i.e., keeping the average composition and ion positions the same. In a random solid solution, the concentration distribution follows the binomial distribution. By comparing the experimental distribution with the binomial distribution, it is possible to calculate the risk of mistaking the experimental data for being non-random, i.e. to erroneously discard the null hypothesis that the experimental distribution is random. FDAs were used in Paper II to statistically confirm the existence of non-randomness in the Si distribution of $\text{Ti}_{0.81}\text{Si}_{0.19}\text{N}$.

6.5 Surfaces and Proximity Histograms

Surfaces of constant concentration or density, so called iso-concentration or iso-density surfaces, can be generated from the voxelated data for a particular ion, group of ions, or ratio of ions, at a value specified by the analyst. This surface can then be used to enhance visualization, identify regions of divergent density from local magnification effects or a pole artefact, define volumes for further analysis, or to find clusters, grain boundaries and other features with compositional or density differences. In Paper II, an iso-density surface was used to identify regions in the APT reconstructions with lower density than the remaining tip. These fluctuations were likely due to uneven heat distribution. In Paper IV, iso-

concentration surfaces showing regions with high Zr content as well as a low non-metal trace element fraction was used to manually assign cylinders for the cylindrical distribution function.

Iso-concentration surface were also used in Papers II and III as starting points for a related data treatment method; the proximity histogram, or proxigram. It works similarly to the RDF, but the starting point is a surface, or a set of surfaces, rather than a particular kind of ion. Instead of measuring radially, the proximity histograms show how the composition changes with distance from the surface in both directions. The error bars are directly related to the number of ions contributing to the measured composition.

6.6 Co-Evaporation Correlation

To better understand the field evaporation characteristics of a specimen, correlations between detected multiple event ions can be investigated. The co-evaporation correlation data is generally investigated using a histogram or a scatter plot, which sometimes is referred to as a Saxey plot [119]. Two such scatterplots are shown in Fig. 6.6.

Fig. 6.6. Co-evaporation correlation scatter plots of a) $\text{ZrB}_{2.0}$ and b) $\text{Ti}_{0.92}\text{Si}_{0.08}^{15}\text{N}$.

Insets show ion pair intersections of interest in greater detail. The opacity of each dot is 5%, except the opaque dots in the $\text{Ti}_2^{15}\text{N}^{3+}$ inset in b).

The m/n of the first and second detected ion in each multiple event generates a semi-transparent dot at the m/n intersection in the scatter plot. Instantaneous and simultaneous field evaporation is common, which results in intense regions close to expected m/n intersections. From these intersections, dots often form straight lines and curved lines. Horizontal and vertical straight lines toward higher m/n are formed by a delay of either the first or the second ion, and can be seen from

most intersections in Fig. 6.6. Delays with respect to the pulse increase the time-of-flight, which in turn is interpreted as a slightly heavier ion, and thus result in a slightly higher m/n . If dots along straight lines are found outside the assigned mass spectrum ranges, only one is properly ranged, but the other can be recovered if it is not overlapping with another m/n intersection.

The directions of the curved lines can be traced back to their origin. Curved lines from intense intersections toward higher m/n are generated from field evaporation where both ions are delayed with regards to the laser or voltage pulse. Ion pairs generating long, curved lines are generally related to two unranged, or improperly ranged, ions [120]. One such long line (from the background) can be seen going through the 19/1 Da intersection in Fig. 6.6 a), while short curved lines toward higher m/n originate in most intense intersections.

Curved lines toward increasing ratio in one axis and decreasing in the other is due to dissociation of molecular ions [119]. A faint example of this is found in Fig. 6.6 b), highlighted by the $\text{Ti}_2^{15}\text{N}^{3+}$ inset. As $^{48}\text{Ti}_2^{15}\text{N}^{3+}$ (37 Da) breaks up into $^{48}\text{Ti}^{15}\text{N}^+$ (63 Da) and $^{48}\text{Ti}^{2+}$ (24 Da) or $^{48}\text{Ti}^{15}\text{N}^{2+}$ (31.5 Da) and $^{48}\text{Ti}^+$ (48 Da), two curved lines are formed between either the 63/24 Da or the 48/31.5 Da intersection and the 37/37 Da intersection. The m/n -values are given for ^{48}Ti , since this is the most abundant isotope of Ti, and thus gives the most prominent line. However, the inset reveals traces of such lines for four out of five stable and abundant Ti isotopes. The position of a dot along a dissociation line depends on when during the time-of-flight the molecular ion dissociates. If dissociation occurs very late in the flight, m/n is largely unchanged from that of the parent ion ($\text{Ti}_2^{15}\text{N}^{3+}$) and the dot is generated close to the intersection of two parent ions (37/37 Da), while early dissociation produces a dot close to the m/n intersection of the two daughter ions.

The co-evaporation correlation scatterplot was important for understanding the field evaporation behavior of ZrB_2 in Paper IV. The lack of ion pairs at intersections along the $x = y$ line, i.e., ion pairs of the same mass-to-charge-state ratio, explain the deviation in the isotopic signature of B in the mass spectra. Moreover, the lack of dissociation tracks from metastable $^{15}\text{N}_2^{2+}$ in co-evaporation correlation scatter plots of TiSi^{15}N further strengthens the assumption that the $^{15}\text{N}_2$ -contribution to the peak at 15 Da in Papers I and II is minimal.

6.7 Compositional Correction Procedures

The field evaporation behavior of ceramics is often correlative, as is described in Section 5.6. The current detector design is not optimized for correlated field evaporation and this may result in preferential losses of ions that exhibit strong correlative field evaporation behavior, which is described in Section 5.7 and shown in Fig. 6.6. The losses are sometimes large enough that the composition must be corrected. One compositional correction procedure was developed in

Paper IV, where it was applied to ZrB_2 and compared with another procedure, as well as the combination of both. The methods cannot correct the ^{15}N content of TiSi^{15}N in Papers I and II, the Al content of ZrAlN in Paper III, or the Ta content of ZrTaB_2 in Paper V, because they all depend on APT measurements of at least two isotopes per element to be corrected, while ^{15}N , Al and Ta are monoisotopic. This is the major drawback of the correction procedures described here. The corrections could, however, be applied to improve the average B/Zr in ZrTaB_2 , but Ta would be underestimated instead of B.

6.7.1 The ^{13}C - and ^{10}B -Method

There is a balance between the isotopes of each element in the periodic system, known as the natural abundance. Each element has a naturally occurring isotopic signature, which describes the relative abundance of each isotope in nature. For stable or very long-lived isotopes, the isotopic signature primarily depends on their abundance when the earth was formed, while the abundance of short-lived isotopes depends on their decay rate. For radiogenic isotopes, i.e., isotopes formed from radioactive decay, the decay rate and total abundance of the parent isotope will also influence the isotopic signature.

In APT, the isotopic signatures are used to assign mass spectral peaks to a specific element or isotope, often referred to as ranging. Deviations in the isotopic signature from that of the natural abundance (or from an abundance measured with another technique) in APT measurements suggests preferential losses of certain isotopes. However, the deviation can also be used to estimate the losses and correct the average composition, even though the spatial coordinates of the isotopes are lost [103,121–123].

Because the magnitude of the peaks in the isotopic signature of both C and B differs, correct background correction of the mass spectrum is necessary in order not to affect the measured isotope ratio, especially in the ^{13}C -method, since $^{12}\text{C}/^{13}\text{C}$ ratio is 99/1. In the case of B, the losses of ^{10}B might not be insignificant since the $^{10}\text{B}/^{11}\text{B}$ ratio is 20/80. This can be corrected for by using an iterative correction of both ^{10}B and ^{11}B until the values stabilize at the selected isotope ratio [123].

6.7.2 Pile-Up Pairs Correction

This new correction method is based on the same principles as the ^{10}B -method, but the correction is applied to the co-evaporation correlation data, rather than the entire specimen. The m/n intersections of ions with similar time-of-flight is often lacking ions due to the detector dead-time/space, also known as pile-up. By using a reference m/n intersection from ion pairs of the same charge state as the intersection to be corrected, an estimated number of lost ions can be acquired. However, two or more isotopes are necessary, since there are no reference intersections for monoisotopic elements. The resulting correction has significantly higher precision for variations in the selected isotope abundance, because only the reference pairs are used as a pivot, rather than the entire

specimen. Although the final composition will depend on the background correction of the mass spectrum, the correction procedure itself does not, in contrast the ^{10}B -method.

6.7.3 Combined Correction

The methods above can also be combined. The pile-up pairs correction is then used to correct the number of ^{10}B ions, which is used as input in the ^{10}B -method to correct ^{11}B . When compared in Paper IV, it yielded more accurate values than the ^{10}B -method, but no significant difference from the iterative ^{10}B -method [123] was found, and the benefits of the pile-up pairs correction, with higher precision and background correction independence, was not retained. It may, however, enable correction with ^{10}B - and ^{13}C -like methods for elements with more complex isotopic signature than C and B, i.e., with more than two isotopes, as each additional isotope makes the iterative method more troublesome to implement.

7. MAIN RESULTS & CONTRIBUTIONS TO THE FIELD

The main scientific and technological advances of my work within the limits of this thesis are presented in this chapter. The impact of these advances is also described.

- ❖ I have shown that isotopic substitution can be used in combination with the analytical technique APT in general, and for TiSiN specifically. In the case of TiSiN I show that the isotopic substitution of ^{nat}N with ^{15}N enables quantitative APT with results in good agreement with ERDA. As discussed in Paper I, the method of isotopic substitution can be applied to a wide range of materials systems that are relevant in many different fields of research.
- ❖ Certain APT data analysis techniques require that the data must first be sampled into voxels, however, the parameters of such samplings are often arbitrarily chosen and based on the experience of the user. I have designed an algorithm for finding the most meaningful sampling parameter, which balances the compositional uncertainty of small sampling volumes with the averaging of small features when the sampling volume is large. This enables visualization of small-scale compositional fluctuations without relying on the experience of the user.
- ❖ I have shown that fluctuations of Si-content exist as domains in $\text{Ti}_{0.81}\text{Si}_{0.19}\text{N}$ films on the scale of ~ 4 nm, which confirm interpretations from analytical TEM. These domains are segregations, preferentially forming pockets between microstructural, columnar features in the film. The APT analyses show no strongly developed SiN_y tissue phase surrounding TiN crystallites. Thus, the films should be characterized as nanostructured rather than nanocomposite. This realization could not be made by analytical high-resolution TEM alone.
- ❖ Paper II concludes that it is the presence of Si on growing TiN grains that gives rise to renucleation and that the Si atoms are trapped in what becomes a mesh of TiN grains only a few nanometers large. These TiN crystallites are at an angle to each other because of an extreme density of dislocations, if not disclinations, caused by the incorporated Si and its preference for tetrahedral bonding to N over octahedral bonding, as in cubic-phase TiN. These findings have impact for understanding the superhardening and high thermal stability of nanostructured TiSiN films because of alloy, defect, and small grain size hardening effects. Since the Si is in the lattice of the TiN phase, the thermal stability of the as-grown

material becomes high. One can envision that otherwise expected grain coarsening and recrystallization is effectively hindered by local increase in Si concentration which is incompatible with growth of the TiN phase and that the development of SiN_y tissue phases would act as diffusion barriers for growth.

- ❖ Paper III shows that the evaporation behavior of Zr_{0.69}Al_{0.31}N is similar to that of TiN-alloys, but with significant local magnification, which prevents quantitative determination of the constituent phases. The self-organization of nanolabyrinthine structures was found to form by surface nucleation after 5-8 nm of film growth with disordered segregation and gradually increasing amplitude until phase separation into alternating lamellae. When grown at 900 °C, the nanolabyrinthine growth was disturbed by nucleation of ZrN grains.
- ❖ The APT study of ZrB₂ in Paper IV provided clear quantitative evidence for B segregation to the column boundaries in stoichiometric and B over-stoichiometric films. Moreover, it revealed the complex field evaporation behavior of AlB₂-type transition metal diborides and motivated the use of APT in the study of ZrTaB₂ in Paper V.
- ❖ The loss of B in ZrB₂ due to correlated evaporation behavior and pile-up in the APT detector lead me to development of a more precise compositional correction procedure that is based on co-evaporation correlation data. This method is not exclusive to borides, and can be applied to all elements with at least two stable and abundant isotopes.
- ❖ Paper V shows that using a hybrid HiPIMS/DCMS technique it is possible to tailor both the metal ratio and the Ta content. Moreover, the characteristics of the column boundaries changes from B-rich to metal- rich, and the hardness as well as the toughness is increased. APT contributed with the quantitative distribution of Ta in Zr_{0.8}Ta_{0.2}B_{1.8}, showing that there often is an increase in Ta at column boundaries, but a significant amount is also found in solid solution within the columns. The study also revealed that the boundaries were B-deficient. The reconstructed atomic density at the column boundaries of ZrB_{2.5} from Paper IV and Zr_{0.8}Ta_{0.2}B_{1.8} from Paper V combined show that the field evaporation of the boundaries compared to the columns varies significantly depending on if they are B- or metal-rich, as is shown in Fig. 5.9 in this thesis.
- ❖ My combined studies of ATP applied to ceramic materials systems resulted in the identification of an artefact previously not described in literature or practice for APT. The artefact manifests as fine lines of higher density in a

pattern similar in shape with MCP multifiber boundaries projected onto the detector. Indications of such lines in detector histograms was found not only for ceramic samples on the specific atom probe instrument, but also in steels analyzed in five different instruments. These observations resulted in Paper VI, where the artefact is described and possible reasons for its occurrence are discussed. The identification of this artefact will lead to reduced risk for misinterpretation and unnecessary deletion of APT data.

8. FUTURE OUTLOOK

- ❖ The detection efficiency of atom probe instruments has recently reached ~80% in a commercial state-of-the-art instrument, compared to ~37% in the instrument used for the studies in this thesis. Increased detection efficiency enables identification of even finer structures, which could be beneficial for resolving the $\text{Ti}_{0.81}\text{Si}_{0.19}^{15}\text{N}$ nanostructure studied primarily in Paper II. A comparison of the data presented in Paper II on $\text{Ti}_{0.81}\text{Si}_{0.19}^{15}\text{N}$ with the same film studied with ~80% detection efficiency could prove very interesting if even more details can be revealed. Since new generation APTs use UV lasers with smaller spot size, this could help prevent heat build-up in the specimens, which may have caused the large-scale density fluctuations in Paper II.
- ❖ The thermal stability of the TiSiN nanostructures studied in Paper II during high temperature annealing could be an interesting topic of exploration, with the as-deposited reference samples already studied. These nanostructures are expected to further phase separate and/or recrystallize. Since the films have been deposited with a TiN diffusion barrier, up-diffusion of W and Co from the substrate should not hinder such a study of the effect of thermal annealing on the nanostructures themselves.
- ❖ The sampling parameter aid developed in Paper I, which has been applied to the data in Papers I, II, and IV-VI, could be automated as well as further improved to use many different combinations of voxel sizes and delocalization parameters.
- ❖ The AlB_2 -structured diborides in Papers IV and V were studied at small angles to the c -axis. Since the analysis direction is known to affect the shape of precipitates and boundaries in APT if the evaporation fields differ [124], such as in the B-rich (Papers IV and V) or metal-rich (Paper V) boundaries compared to the columnar grains, the width of the boundaries could be more accurately determined if analyzed perpendicular to the growth direction (and c -axis). In addition, in Paper IV I theorize that the relatively low multiple events percentage, high mass resolution, and lack of molecular ions and mutually delayed ion pairs in ZrB_2 could be a result of the present crystal structure and orientation of the specimens, which results in a structure of alternating layers of close-packed Zr and graphene-like B with surface normal at small angles to the analysis direction.

- ❖ The new pile-up pairs correction procedure that I developed and applied in Paper IV seems promising, with significantly better precision, as well as very good accuracy in the most homogeneous film. To determine whether the lack of accuracy when applied the heterogenous film is due to the reference value from ERDA or the correction procedure itself, the pile-up pairs correction should be applied to a set of samples with known and homogeneous composition, thereby measuring its accuracy. In addition, the method could be refined by retrieving data from simultaneous, but delayed multiple ions [119,120], to be as accurate as possible for materials with less ideal co-evaporation correlation characteristics than ZrB₂.
- ❖ In Paper VI, I found that the MCP of a particular atom probe instrument influenced the spatial distribution of the detection efficiency, resulting in regular lines of higher-than average density along the analysis direction for some detector coordinates. Increased detection efficiency in the same pattern was found in data from five atom probe instruments out of the seven tested. In order to determine how wide-spread this artefact is in terms of models and number of affected instruments, suitable data from more atom probe instruments of different models should be studied.
- ❖ New and interesting reconstruction algorithms, which take local magnification into account by not restraining the equilibrium surface to hemispherical, are under development [106,107]. Once mature, these could be applied to existing APT raw data known to exhibit strong local magnification, in particular ZrAlN in Paper III, but also ZrB₂, and Zr_{0.8}Ta_{0.2}B_{1.8} in Papers IV and V, possibly revealing new information regarding the distribution of elements and the influence of local magnification when using conventional reconstruction algorithms.
- ❖ Most of the specimens studied by APT in this thesis have such small grains that they can be said to be boundary dominated. This applies to the small grains of the Ti_{0.81}Si_{0.19}¹⁵N films in Papers I and II, the thin lamellae of Zr_{0.68}Al_{0.31}N in Paper III, as well as the fiber-textured ZrB₂ and ZrTaB₂ studied in Papers IV and V, respectively. Grain boundaries are known to influence the local field evaporation [104,105], and in these specimens there are no regions even close to bulk. Such a grain boundary effect in APT could be studied by comparing one or more boundary dominated films with a high-quality single-crystal film of the same material, e.g., TiN. Such a study could be helpful in understanding the role of grain size and boundaries in the field evaporation of ceramics.

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Paper I

Resolving Mass Spectral Overlaps in Atom Probe Tomography by Isotopic Substitutions – Case of TiSi^{15}N

Paper II

Solid Solution and Segregation Effects in Arc-Deposited $\text{Ti}_{1-x}\text{Si}_x\text{N}$ Thin Films Resolved by ^{15}N Isotopic Substitution in Atom Probe Tomography

Paper III

Self-Organized Nanostructuring in $\text{Zr}_{0.69}\text{Al}_{0.31}\text{N}$ Thin Films Studied by Atom Probe Tomography

Paper IV

Atom Probe Tomography Field Evaporation Characteristics and Compositional Corrections of ZrB_2

Paper V

Strategy for Simultaneously Increasing Both Hardness and Toughness in ZrB_2 -rich $\text{Zr}_{1-x}\text{Ta}_x\text{B}_y$ Thin Films

Paper VI

Observations of Atomic Density Artefacts in Atom Probe Tomography from Microchannel Plate Multifiber Boundaries

Papers

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