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Transition metal carbide nanocomposite and amorphous thin films

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The cover image shows a high resolution transmission electron microscopy image of a nanocomposite structure consisting of crystalline titanium carbide grains in an amorphous matrix of silicon and carbon. On the backside part of a selected area electron diffraction pattern from the same film is also seen.

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Abstract

This thesis explores thin films of binary and ternary transition metal carbides, in the Nb-C, Ti-Si-C, Nb-Si-C, Zr-Si-C, and Nb-Ge-C systems. The electrical and mechanical properties of these systems are affected by their structure and here both nanocomposite and amorphous thin films are thus investigated. By appropriate choice of transition metal and composition the films can be designed to be multifunctional with a combination of properties, such as low electric resistivity, low contact resistance and high mechanical strength. Electrical contacts are one example of application that has been of special interest in this thesis. Since some industrially important substrates used in electrical contacts soften at higher temperature, all films were deposited with dc magnetron sputtering at a low substrate temperature (200-350 °C).

I show that the electrical resistivity and mechanical properties of composites consisting of nanocrystalline NbC grains (nc-NbC) in a matrix of amorphous C (a-C) depend strongly on the amount of amorphous C. The best combination of hardness (23 GPa) and electrical resistivity (260 $\mu\Omega\cdot\text{cm}$) are found in films with ~15 at.% a-C phase. This is a higher hardness and lower resistivity than measured for the more well studied Ti-C system if deposited under similar conditions. The better results can be explained by a thinner matrix of amorphous C phase in the case of NbC. The nc-NbC/a-C is therefore interesting as a material in electrical contacts.

Si can be added to further control the structure and thereby the properties of binary Me-C systems. There are however, different opinions in the literature of whether Si is incorporated on the Ti or C site in the cubic NaCl (B1) structure of TiC. In order to understand how Si is incorporated in a Me-Si-C material I use a model system of epitaxial TiC_x ($x \sim 0.7$). In this model system a few atomic percent of Si can be incorporated in the cubic TiC structure. The experimental results together with theoretical stability calculations suggest that the Si is positioned at the C sites forming $\text{Ti}(\text{Si},\text{C})_x$. The calculation further shows a strong tendency for Si segregation, which is seen at higher Si contents in the experiments, where Si starts segregate out from the TiC_x to the grain boundaries causing a loss of epitaxy.

If Si is added to an Nb-C nanocomposite, it hinders the grain growth and thus a reduced size of the NbC grains is observed. The Si segregates to the amorphous matrix forming a-SiC. At the same time the resistivity increases and the hardness is reduced. With even higher amounts of Si (>25 at.%) into the Nb-Si-C material, grain growth is no longer possible and the material becomes amorphous. In order to separate between effects from the addition of Si and the choice of transition metal I compare the Nb-Si-C system to already published results for the Zr-Si-C system. I find that the hardness of the material depends on the amount of strong

Si-C bonds rather than the type of transition metal. The reduced elastic modulus is, however, dependent on the choice of transition metal. I therefore suggest that it is possible to make Me-Si-C films with high wear resistance by an appropriate choice of transition metal and composition.

Electron microscopy was of importance for determining amorphous structures of Nb-Si-C and Zr-Si-C at high Si contents. However, the investigations were obstructed by electron beam induced crystallization. Further investigations show that the energy transferred from the beam electrons to C and Si atoms in the material is enough to cause atomic displacements. The displacements cause volume fluctuations and thereby enhance the mobility of all the atoms in the material. The result is formation of MeC grains, which are stable to further irradiation.

Finally, I have studied substitution of Ge for Si in a ternary system looking at Nb-Ge-C thin films. I show that the films consist of nc-NbC/a-C/a-Ge and that Ge in a similar way to Si decreases the size of the crystalline NbC grains. However, a transition to a completely amorphous material is not seen even at high Ge contents (~30 at.%). Another dissimilarity is that while Si bonds to C and forms a matrix of a-SiC, Ge tends to bond to Ge.

Populärvetenskaplig sammanfattning

Tunna filmskikt för bättre materialegenskaper

Ett material kan beskrivas med en eller flera karaktäristiska egenskaper. Järn är till exempel hårt, men rostar lätt i fuktiga miljöer. För att skydda järn från rost kan man tillsätta andra grundämnen så att rostfritt stål bildas. Alternativt målas järnet med en rostfri färg. I min forskning applicerar jag ett tunt skikt som inte tjockare än 1/100 av diametern på ett hårstrå av ett material ovanpå ett annat för att förändra egenskaperna på ytan. Liksom man inte bara väljer färg efter dess vädertålighet utan även dess kulör, kan man ofta kombinera flera olika önskvärda egenskaper genom ett smart val av olika grundämnen i sitt tunna filmskikt. Själv försöker jag hitta ett material som ska fungera bra i en elektrisk kontakt, som i exempelvis en mobiltelefonladdare. Här behöver vi kombinera skydd mot oxidation med god ledningsförmåga och nötningstålighet. Målet med forskningen är att kunna byta ut de ämnen som ofta används idag (silver och guld), vilka både är dyra och ofta beläggs i processer som använder miljöfarliga kemikalier. Nu ska beläggningarna ske i vakuum och med renast möjliga förhållanden.

Ett material som redan har visat sig fungera som tunnfilm på elektriska kontakter är en kombination av titan och kol. Detta material består av små hårda korn av titankarbid omgivna av mjukare kol (ungefär som en småkaka med chokladbitar i). Jag har i min forskning prövat att byta ut titan mot niob eftersom dessa grundämnen ligger nära varandra i det periodiska systemet och har liknande egenskaper. Den skillnad jag upptäckte är att det i filmer innehållande niob finns mindre omgivande kol. (Samma mängd chokladbitar, men mindre kaksmet.) Detta är fördelaktigt om man vill leda ström genom filmen eftersom kolet inte leder ström så bra. Min slutsats är därför att niob-kol-materialet fungerar minst lika bra som titan-kol när det gäller att tillverka en elektrisk kontakt.

Ibland kan det vara nödvändigt att tillsätta ett tredje grundämne för att ytfilmen ska få alla de egenskaper man önskar. Det är i så fall viktigt att förstå var detta grundämne sätter sig och hur strukturen i materialet förändras. I min forskning handlar det om att tillsätta kisel i titankarbid. I ren titankarbid sitter titan- och kolatomerna på ett välordnat sätt. Om man sedan tillsätter små mängder kisel så sätter sig kiselatomerna på samma plats som kolatomer skulle gjort och strukturen bevaras. Kiselatomer vill dock hellre sitta utanför titan-kol-strukturen. Med större mängder kisel bryts därför den välordnade strukturen sönder. Kvar blir mindre korn av titankarbid. Inne i dessa sitter titan- och kolatomer fortfarande på ett välordnat sätt. Runtom kornen sätter sig kisel- och kolatomer på ett helt oordnat sätt. Ju mer kisel desto mindre blir kornen. Kisel kan därför användas till att styra kornstorleken och därmed påverka till exempel hårdheten i detta material.

Samma förändring i strukturen sker med tillsatser av kisel i niobkarbid. Om antalet kiselatomer är fler än en fjärdedel av det totala antalet atomer förloras strukturen helt och samtliga atomer hamnar på ett slumpmässigt och oordnat sätt. Ett glasartat, s.k. amorft, material skapas då. Detta är inte till någon fördel för de elektriska egenskaperna eftersom det inte finns någon välordnad struktur där strömmen enkelt kan ta sig fram, men bra ur ett perspektiv där det handlar om att skydda det underliggande materialet mot till exempel nötning.

För att beskriva strukturen och detaljerna hos mina material har jag studerat dem med atomär upplösning i ett transmissionselektronmikroskop (TEM). Detta mikroskop fungerar på samma sätt som vanligt ljusmikroskop, men i stället för synligt ljus använder jag mig av elektroner för att avbilda materialet. Att jag använder mig av elektroner beror på att dessa kan ge en högre upplösning än synligt ljus. I princip fås en bättre upplösning ju högre energi elektronerna har och därför använder jag elektroner med mycket hög energi. Faran är dock att en del av denna energi överförs till materialet och förändrar strukturen.

Jag har därför undersökt elektronstråle-inducerade förändringar i filmer av zirkonium-kisel-kol och niob-kisel-kol. Från början sitter atomerna i dessa material helt oordnat men efter några minuters elektronbestrålning bildas korn av zirkonium-kol respektive niob-kol. Det är därför viktigt att vara observant om man studerar denna typ av material i elektronmikroskop. Genom flera olika experiment kom jag fram till att förändringarna beror på att kol- och eventuellt kiselatomer kan flytta på sig om en elektron skulle kollidera rakt in i en sådan atomkärna. För att undvika denna typ av skador kan man antingen sänka energin hos de inkommande elektronerna för att förhindra skadan eller vara så snabb i exponeringen att provet inte hinner påverkas.

Preface

I here present the outcome of my years of work as a PhD-student in the Thin Film Physics Division at Linköping University. The thesis has been performed within Theme 1 of the VINN Excellence Center on Functional Nanoscale Materials (FunMat). The research was carried out in cooperation with Uppsala University, Technical Research Institute of Sweden (SP), and the companies Impact Coatings AB and ABB AB. The present PhD Thesis is an expansion of my Licenciate Thesis (No. 1561, Linköping Studies in Science and Technology), which was presented in December 2012.

Included papers

Paper 1

Structural, mechanical and electrical-contact properties of nanocrystalline-NbC/amorphous-C coatings deposited by magnetron sputtering

N. Nedfors, **O. Tengstrand**, E. Lewin, A. Furlan, P. Eklund, L. Hultman, U. Jansson

Surface and Coatings Technology 206 (2011) 354-359

Paper 2

Incorporation effects of Si in TiC_x thin films

O. Tengstrand, N. Nedfors, B. Alling, U. Jansson, A. Flink, P. Eklund, L. Hultman.

Manuscript in preparation

Paper 3

Characterization of amorphous and nanocomposite Nb-Si-C thin films deposited by DC magnetron sputtering

N. Nedfors, **O. Tengstrand**, A. Flink, P. Eklund, L. Hultman, U. Jansson

Thin Solid Films 545 (2013) 272-278

Paper 4

Beam-induced crystallization of amorphous Me-Si-C (Me = Nb or Zr) thin films during transmission electron microscopy

O. Tengstrand, N. Nedfors, M. Andersson, J. Lu, U. Jansson, A. Flink, P. Eklund, L. Hultman

MRS Communications 3(3) (2013) 151-155

Paper 5

Model for electron-beam-induced crystallization of amorphous Me-Si-C (Me = Nb or Zr) thin films

O. Tengstrand, N. Nedfors, M. Andersson, J. Lu, U. Jansson, A. Flink, P. Eklund, L. Hultman

Manuscript in preparation

Paper 6

Structure and electrical properties of Nb-Ge-C nanocomposite coatings

O. Tengstrand, N. Nedfors, L. Fast, A. Flink, U. Jansson, P. Eklund, L. Hultman

Manuscript in preparation

My contribution to included papers

Paper 1

I carried out all TEM characterization and contributed to writing the paper.

Paper 2

I took part in the planning of the work, performed most of the experimental work, analyzed the results and wrote the paper. I discussed the simulation structures with Björn Alling, who performed the theoretical calculations.

Paper 3

I carried out all TEM characterization and contributed to writing the paper.

Paper 4

I was responsible for planning the work, performed most of the experimental work, analyzed the results, and wrote the paper.

Paper 5

I was responsible for planning the work, performed most of the experimental work, analyzed the results, and wrote the paper.

Paper 6

I took part in the planning of the work, performed most of the experimental work, analyzed the results, and wrote the paper.

Related papers not included in the thesis

Paper 7

Phase-stabilization and substrate effects on nucleation and growth of $(\text{Ti}, \text{V})_{n+1}\text{GeC}_n$ thin films

S. Kerdsonpanya, K. Buchholt, **O. Tengstrand**, J. Lu, J. Jensen, L. Hultman, P. Eklund

Journal of Applied Physics 110 (2011) 053516

Paper 8

Discovery of the ternary nanolaminated compound Nb_2GeC by a systematic theoretical-experimental approach

P. Eklund, M. Dahlqvist, **O. Tengstrand**, L. Hultman, J. Lu, N. Nedfors, U. Jansson, J. Rosén

Physical Review Letters 109 (2012) 035502

Paper 9

Reactive sputtering of NbC_x -based nanocomposite coatings: an up-scaling study

N. Nedfors, **O. Tengstrand**, A. Flink, P. Eklund, L. Hultman, U. Jansson

Manuscript in preparation

Paper 10

Superhard NbB_{2-x} thin films deposited by dc magnetron sputtering

N. Nedfors, **O. Tengstrand**, J. Lu, P. Eklund, P.O.Å. Persson, L. Hultman, U. Jansson

Submitted for publication

Paper 11

Study of Nb-B-C thin films for electrical contact applications deposited by magnetron sputtering

N. Nedfors, **O. Tengstrand**, P. Eklund, L. Hultman, U. Jansson

Manuscript in final preparation

Paper 12

Si incorporation in $\text{Ti}_{1-x}\text{Si}_x\text{N}$ films grown on $\text{TiN}(001)$ and (001) -faceted $\text{TiN}(111)$ columns

A.O Eriksson, **O. Tengstrand**, J. Lu, J. Jensen, P. Eklund, J. Rosen, I. Petrov, J. E. Greene, L. Hultman

Submitted for publication

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In some sense I feel sad for finishing, since this marks the ending of something that have been a most interesting part of my life during the past five years. In other ways I feel relieved that it's over. Most of all I think I'm excited about the future. I hope to meet you there!

/Olof

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1 Introduction

1.1 Background to my work

Thin films[†] are deposited onto a substrate to enhance or add properties to the combined material system. Depending on the intended use, the thickness of the films can range from a few atomic layers to several micrometers. Thin films can be used for purely decorative purposes as in the case of earliest known use where the Egyptians hammered gold into leaves with a thickness below 1 μm [1]. However, combining different substrate and thin film materials gives the opportunity to tailor also other system properties. Today, thin films are therefore wide spread and used for a large variety of purposes. For example, there are anti-reflective coatings for eyeglasses and hard coatings to increase the wear-resistance of cutting tools.

Coatings are also often used in electrical contact applications [2-7]. This is done mainly to protect the contact from oxidation and to lower the contact resistance. Two common materials for contact applications are the noble metals Au and Ag [8,9]. Au has a good oxidation resistance, but is expensive. Ag is less expensive, but tends to tarnish in the presence of sulfides or chlorides [10,11]. It is therefore motivated to replace noble metals with other coatings.

An interesting class of materials in this aspect is multicomponent transition metal carbides [6,12-15]. When deposited at low process temperatures, these materials tend to form nanocomposites, which consist of at least two phases, segregated on the nanoscale. Two well-studied examples are the Ti-C and Ti-Si-C systems which have already been shown to have promising electrical [13,16,17] and tribological [18-20] properties. These properties are controlled by the microstructure and the material can therefore be tailored by the choice of composition and deposition conditions [20-22].

Although both the tribological and electrical properties of Ti-Si-C-based nanocomposites have already been investigated, information on how Si is incorporated

[†] Sometimes the word *coating* is also used in the field. In some contexts this word is used for *thin films* thicker than $\sim 1 \mu\text{m}$. In other contexts the word *coating* is used for all deliberately added layers, while films are referring to thin layers of contamination. In this thesis both the terms *coating* and *thin film* are used for deliberately deposited layers.

in the NaCl-structure TiC_x phase has been lacking. I have therefore aimed for deeper understanding of this by investigating a model system of epitaxial TiC_x . The model system also shows how Si segregates to form a composite material at low temperatures. Also other transition metal carbides have been studied. In the case of Nb-C, the system was screened and by Lewin [23] and proposed as a candidate for electrical contact applications. Here, I investigate the system in more detail with respect to microstructure as well as electrical and mechanical properties. I find that it is at least as good as the Ti-C system for electrical contact applications.

The addition of a Si does not only add to the complexity of the system, but also allow further possibilities to tailor the properties. Results from the Zr-Si-C system show that the hardness of the films is related to the amount of Si-C bonds and that amorphous films form for Si contents larger than 15 at.% [24]. Since sputter-deposited films in the Nb-Si-C system have not been studied earlier I here investigate this system and compare the results with the Zr-Si-C system in order to separate the effects of Si and choice of transition metal.

Lauridsen et al. [14] investigated different A-elements ($A = \text{Si}, \text{Ge}$ or Sn) in Ti-A-C-Ag coatings for electrical contact applications. The results show that Ge gave a dense structure and the lowest contact resistance among the investigated coatings. In combination with our promising results for the Nb-C system as electrical contact I therefore investigated the Nb-Ge-C material system. Since I also want to compare the system with some of our results for the Nb-Si-C, I increased the Ge content up to 30 at.%. My Nb-Ge-C coatings are, however, porous, which is not a good condition if they are going to be used in a corrosive environment.

Many of the findings of my work are related to the film microstructure as determined by high resolution transmission electron microscopy (TEM). In TEM investigations artifacts can be induced by both sample preparation and imaging [25-27]. While carefully performed sample preparation techniques can be used to obtain electron transparent samples for my samples without introducing artifacts, electron-beam-induced damage, however, proved a challenge. I found that amorphous Nb-Si-C coatings crystallize under electron beam irradiation. Therefore, I developed a method with indicated times allowed to record images of the pristine amorphous structure, and also to monitor the electron-beam-induced crystallization as well as to describe the mechanisms behind it. I also added the related Zr-Si-C system to see how the crystallization is related to the choice of transition metal.

1.2 Objective

The aim of my work is to relate the properties of transition metal carbides to the structure and composition of the materials. The main focus has been on material systems that have potential for electric contact application. In some cases, however, the compositional range have been extended beyond what is useful for

electrical contacts in order to further investigate, for example, how mechanical properties is related in amorphous structures.

A second aim has been to investigate and explain the electron-beam-induced crystallization in the amorphous phase of these materials.

1.3 Outline

I have chosen to divide the part prior to my papers into 7 chapters, which treat different aspects of my work. The next chapter gives an introduction to electrical contacts. Chapter 3, in more detail describes the different investigated material systems together with the different microstructures observed from compositional changes. For all thin films, I have used a deposition technique called magnetron sputtering. The physics behind this method together with the special conditions required for it to work are described in chapter 4. Chapter 5 treats some of the used characterization methods. Since a key contribution of my work is to characterize electron-beam-induced crystallization in amorphous materials, I extensively describe this phenomenon in chapter 6. Finally I summarize my contribution to the field in chapter 7.

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2 Electrical contacts

Electrical contacts are of importance for this thesis since my collaboration with the industrial partners in the VINNEX Center *FunMat* Theme 1 deals with the development of coatings[†] for electrical contact applications. This is reflected in **Papers 1** and **6**, where we investigate how the microstructure influences electrical properties of Nb-C and Nb-Ge-C coatings, respectively. The following chapter gives a brief introduction to the function of electric contacts and available contact materials. More detailed description of electrical contact theory can be found, e.g., in texts written by Holm [1], Slade [2], and Braunovic [3].

Fig. 2.1 Schematic figure of the cross-section (left) and plan view (right) of an electrical contact. (After Lewin [4])

An electrical contact is according to the definition by Holm [1] “a *releasable junction between two conductors which is apt to carry electric current*”. This means two surfaces (contact members) that when in contact with each other are able to carry electrons from one of the contact members (cathode) to the other

[†] Note that in the field of electrical contacts the terms *film* or *thin film* is often referring to a contamination layer formed on top of the contact. To avoid confusion these terms are not used in this chapter.

contact member (anode). However, the surface interaction between the contact members can be very complex. This is illustrated in **Fig. 2.1**, which shows schematic figures of an electrical contact in cross-section (left), and plan-view (right). This contact consists of one coated and one uncoated part, which are pressed together by a contact force. Although the apparent contact area, A_{apparent} , may seem large, surface roughness will reduce the actual load bearing area, A_{load} , where an electric current can flow. If the materials also include non-conducting phases, e.g., an insulating oxide on the surface, the actual conductive area, $A_{\text{conductive}}$, will consist only of the small areas where the contact pressure is high enough to break through the oxide. The conducting spots out of which $A_{\text{conductive}}$ consists are called a-spots. At an a-spot the electrical current flux is much higher than in the bulk of the contact. This gives rise to a constriction resistance in the contact. The total constriction depends on the area and distribution of the a-spots. The contact resistance, which is an important property of all electrical contacts, is mainly caused by the constriction resistance. Therefore the contact resistance is not only a property of the contact material, but also of the application (e.g., force applied) and surface contamination.

Electrical contacts are found in all electrical systems. The requirements on these contacts are different depending on in which regime they are supposed to work, e.g., at high or low contact force, and how their mechanism is designed, e.g., sliding or permanent contact. Except for being a good electrical conductor and having a low contact resistance, contact materials also have to be corrosion resistant and ductile. In this thesis possible applications for the investigated material systems, Nb-C and Ti-Si-C, involve non-static contacts. This adds wear resistance and low friction to already mentioned properties.

The electrical and mechanical properties of the top surface are often the most crucial part in electrical contacts. A contaminated surface will increase the contact resistance and reduce performance of the contact. Therefore, contacts are often coated. Not only the functionality of the coating is of importance, but also the adhesion to the substrate, the cost, and the environmental impact of the deposition must be considered.

The dominant method of producing electrical contact coatings today is by plating. In electroplating metal ions are deposited onto a conductive surface from an electrolytic bath. Electroplating can be used for dense coatings. Another plating method is a chemical reduction process called electroless plating. In the process coating growth will occur on a activated surface immersed in the plating solution. Both methods can be used for complex shapes. However, there are limitations for which materials and compositions that can be used. There is also an environmental issue with dangerous chemicals from the plating bath.

An alternative method that is used for the coatings presented in this thesis is physical vapor deposition, PVD (see **Ch. 4** for a more detailed description of this method). The main advantage over plating is that a much wider range of materials and compositions can be deposited. PVD is also a more flexible technique for

changing between different coating materials in the deposition system and is more environmental friendly. One disadvantage is that the method is non-selective, which means that the coating material will be deposited also on, e.g., the chamber walls. This can result in a waste of expensive coating materials.

As substrate material for electrical contact coatings Cu-based alloys are often used, e.g., brass or bronze. Cu is used since it is relatively inexpensive and at the same time has very good electrical and thermal conductivity. The drawback is a relatively low deformation temperature (200-300 °C) [3]. A diffusion barrier of Ni is often used to hinder the Cu from diffusing through the top coating and to serve as load support. The top coating is often a noble metal or alloy in order for the contact resistance to remain low and stable over the lifetime of the contact. An alternative to Cu-based alloys is stainless steel, which is cheaper than Cu and has good corrosion properties.

Among the noble metals, Au has the best resistance against oxidation, but is at the same time a very soft metal. It is therefore a very good contact material for low-current and low contact force applications [5] such as mobile phones and other hand-held electronics. Adding small amounts of Ni and Co increases hardness and wear resistance. These alloys are therefore often called hard gold. The main drawback with Au is the high price and negative environmental impact when deposited by electro plating.

A less expensive alternative to Au is Ag. Ag has the lowest electrical resistivity and highest thermal conductivity of all elements. However, if Ag is exposed to sulfides [6] or chlorides [7] it will tarnish and form a contamination layer that will decrease the performance. To protect Ag from tarnish it can be alloyed with Pd [8], but at a much higher production cost of the coating.

The high price of Au and the tarnishing of Ag motivate a search for new materials. In order to allow for tribological improvements and at the same time retain good electrical properties, nanocomposite materials have been investigated. Special interests have been paid to binary and ternary systems of transition metals and carbon, such as Ti-C and Ti-Si-C [9-12]. These systems often consist of metal-carbon grains in a matrix of amorphous C. The properties can be controlled by the structure, e.g., grain size and matrix thickness, as well as the choice of metal [13-15]. Most nanocomposite coatings can be deposited at low temperatures and are therefore useful for industrial substrates such as Cu, which softens already at ~200 °C [3]. Studies to scale up the deposition process to meet industrial demands such as larger deposition areas and higher deposition rates have been successful [9-10].

However, to be able to develop new nanocomposite materials for electrical contact applications a further understanding on how the structure and composition affects the properties is needed. This is as mentioned in the beginning of this chapter done with the Nb-C system in **Paper 1**, where I show how the microstructure influences electrical properties.

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been indexed 1 and 2 and the mirror plane is drawn by a vertical dotted line. The substrate pattern is not included in this figure.

The word *composite* means that the material consists of at least two phases. Each phase can be amorphous or crystalline and consist of one or more elements. **Fig. 3.2 b)** shows an example taken from **Paper 2** of a sample from the Ti-Si-C system, where crystalline TiC grains are embedded in a matrix of amorphous C and SiC. This is often written as c-TiC/a-C/a-SiC. To emphasize that the size of the crystalline TiC grains are smaller than 100 nm in one or more dimensions (i.e. are nano-crystalline [1]) “nc-“ is added to TiC so it now reads nc-TiC/a-C/a-SiC. In the same way a system is called a *nanocomposite* when one or more of its phases are restricted to a size less than 100 nm in at least one dimension.

Fig 3.2 Different observed microstructures a) epitaxial, b) composite, and c) amorphous.

By definition the atoms in an *amorphous* material are distributed without any long range order between them as shown in **Fig. 3.2 c)**. In practice the interpretation of an amorphous material is often more unclear. With X-ray amorphous we mean a material, which does not give any or very broad peaks in such diffraction measurements. However, these materials can still contain crystalline grains of the order of a few nanometers. Even when viewed in high resolution TEM there can be a problem to distinguish between amorphous and nanocrystalline materials since also the former material type can have a short-range order [2]. An example of this kind of short range order is marked with a circle in **Fig. 3.2c)**. In **Paper 4** and **5** I consider materials with crystalline particles larger than ~1.5 nm to be nanocrystalline and materials with areas with short-range order smaller than this amorphous.

3.2 Me-C

The metal carbides studied in this thesis belong to the refractory carbides. They all share properties like high hardness and high melting point together with semimetallic electrical conductivity [3]. Hägg formulated an empirical rule for the formation of interstitial carbides [4]. The rule states that if the atomic radii carbon-to-metal ratio is smaller than 0.59 interstitial carbides form where carbon occupies the largest interstitial sites in the metal crystal structure. The difference between an interstitial carbide and a solid solution is that the metal crystal structure changes when forming an interstitial carbide while the structure remains the same if carbon is dissolved interstitially and form an solid solution. The structure of the interstitial carbides results in a combination of ionic, covalent and metallic bonds [5].

Fig. 3.3 Structure of the metal carbides in this thesis. Smaller atoms are C located at the interstitial octahedral sites of the Me fcc lattice.

All metals studied in this thesis fulfill the Hägg rule [4] and form carbides in the NaCl (B1) structures as shown in **Fig. 3.3** with C at the interstitial octahedral sites of the Me fcc lattice. For Ti and Zr, this is the only carbide phase, while for Nb there also exists an $\text{Nb}_2\text{C}^\dagger$ phase [4].

The B1 phases can be non-stoichiometric and therefore often written as MeC_x , where x is the carbon to metal ratio. The stability range is wide with 0.47-0.97 [7], $0.72 < x < 1.0$ [4], and $0.61 < x < 1.0$ [8], for Ti, Nb, and Zr, respectively. The carbon content has a large influence on the lattice parameter [6], which changes parabolically. The smallest value for the lattice parameter is found at the lowest value of x in the stability range. For the Zr and Ti carbides, the largest lattice parameter is, however, not at maximum x .

[†] This phase has a narrow range of existence at low temperatures [6], and probably due to the relatively high carbon content in my films, it was never observed in this thesis.

With increasing carbon content the excess C starts to form an amorphous phase turning the MeC system into a two-phase system of nc-MeC_x/a-C. This is possible even before x reaches its maximum value. In TiC_x for example, an a-C phase starts to form already around x > 0.7 [4,5]. When epitaxial TiC films are grown in **Paper 2** we therefore try to keep x below this value. Even higher carbon content reduces the grain size further and the amount of a-C matrix increases.

Not only the structure, but also mechanical and electrical properties change with the C content. The properties are affected by both the understoichiometry and the amount of free carbon. The carbon vacancies in the MeC_x will lead to higher amounts of electron scattering which increases the electrical resistivity with smaller x [3,9]. At the same time loss of strong covalent bonds decreases the hardness of the material with decreasing x [3]. For the nc-MeC_x/a-C nanocomposite, increasing carbon content can at first increase the hardness due to the formation of smaller grains. The a-C matrix is in itself, however, softer than the MeC_x grains. Hence, with even higher carbon content a thicker matrix softens the coating by its presence and the fact that the grains can glide and rotate to a larger extent. Since the amorphous matrix does not conduct an electrical current as well as the MeC_x grains, the electrical resistivity is increased with increased amount of a-C. The resistivity is in this case also increased by a larger amount of grain boundary scattering of electrons due to the formation of smaller MeC_x grains.

Paper 1 describes the effect of the C/Nb ratio in NbC nanocomposite films. The NbC system was selected on the basis of preliminary results from Lewin, [10] who studied several different MeC intended for electrical contact application, and found NbC as a possible candidate. The results are compared to TiC nanocomposites with the same composition since this material previously has shown interesting results as electrical contact material [11,12]. Smaller grains and less free carbon in the NbC system for a given C/Me ratio, give a thinner amorphous matrix and a higher value of x in the MeC_x. This leads to contact properties of the Nb-C composite that are at least as good or better as Ti-C.

3.3 Me-Si-C

The complexity of the binary metal carbide system increases substantially at the addition of a third element. Depending on the composition, temperature, and type of growth template the structure of the Me-Si-C materials can form a solid solution, two- or multiphase materials, nanocomposite, amorphous, or nanolaminate structures (see below). Since the properties and the structure depend to large extent on both Si and C content [13-15], also the ability to design and combine several different desired properties into a multifunctional material increases for the ternary system. Early transition metal silicon carbide thin films have therefore been studied for use in a wide range of different applications such as protective coatings [16-18], electrical contacts [19], solar cells [20], and thermal printing heads [21].

One reason to consider the Me-Si-C systems is the possibility of forming so called MAX phases. By a broader definition MAX phases are a group of inherently nanolaminated materials consisting of an early transition metal (M), a group A element and either C and/or N (X) [22]. This class of materials has been reported to have an interesting combination of metallic and ceramic properties [23]. Of the different Me-Si-C systems investigated in this thesis it is Ti-Si-C that has been reported to form a MAX phase (Ti_3SiC_2) [22]. This MAX-phase was measured to have good electrical and thermal conductivity, together with corrosion and heat resistance [23-26], which is of interest for electrical contact applications. Since the diffusivity of atoms needs to be high in order to form the rather large unit cell ($\sim 17.7 \text{ \AA}$ c-axis), high substrate temperatures ($>700 \text{ }^\circ\text{C}$) are usually required in order to deposit a MAX phase structure [19,25]. This is problematic in some industrial processes due to the heat sensitivity of several industrially relevant substrates (e.g., steel and Cu) [27]. Because of these requirements of lower deposition temperatures, I have in this thesis not been directly concerned with the MAX phase formation.

At temperatures below $700 \text{ }^\circ\text{C}$, cubic MeC are normally observed as the main crystalline phase although other phases such as metal-silicides have also been observed in XRD [25,28,29]. The solubility of Si in the cubic MeC_x is low (less than a few at.%) [5,30] and at higher concentrations Si therefore segregates to grain boundaries. This Si segregation disturbs the growth of MeC crystalline grains and reduces the grain size compared to the binary systems. The resulting microstructures of Me-Si-C thin films deposited by magnetron sputtering thus typically consist of nanocomposites, with nanometer sized metal carbide grains (nc-MeC) in an amorphous matrix of C or SiC (a-C/a-SiC) [16,18,19,25,31,32].

Understanding how the Si interacts with the MeC and segregates to form a composite material is an important key to be able to explain the properties of the formed materials. Suggestions on the position of Si dissolved in TiC_x have been made for both the C [33,34] and Ti [35-37] sites. In **Paper 2** a model system of epitaxial TiC_x ($x \sim 0.7$) is used to investigate how low contents of Si is gradually incorporated in the structure. The experiments are combined with theoretical stability calculations. The results show that Si sits preferentially on the C sites in the TiC structure. However only a few at.% Si can be incorporated before the epitaxy breaks down and a nanocomposite structure of nc-TiC/a-SiC is formed.

Amorphous phases can usually form at higher Si contents and at least X-ray amorphous films have been observed in several different Me-Si-C systems [15, 21,38,39]. The amount of Si required to form a completely amorphous system is dependent on the metal. For Zr, which is known for having a glass-forming ability the required Si content is $\sim 15 \text{ at.}\%$ for dc magnetron sputtering at $350 \text{ }^\circ\text{C}$ [38]. Under similar deposition conditions I found in **Paper 3** that the glass transition for Nb-Si-C is $25 \text{ at.}\%$ Si and from depositions of Ti-Si-C thin films I observe retained nanocrystallinity for up to $30 \text{ at.}\%$ Si in Ti-Si-C thin films. However, the deposition condition also seems to be of importance. If, for example, cooled substrates [15] or a close distance between substrate and target [31] are used magnetron sputtering can result in Ti-Si-C films that are amorphous in HRTEM.

The energetic electron irradiation during TEM studies can induce crystallization in amorphous Nb-Si-C and Zr-Si-C samples. In **Paper 4** I show that displacements of atoms are the cause of this crystallization. (See more details on electron induced crystallization in **Ch. 6**.) **Paper 5** shows that a higher Si content to a small extent can stabilize the amorphous structures against electron-beam-induced crystallization. However the largest difference in stability is due to the choice of transition metal. Zr-Si-C films are more stable than Nb-Si-C films.

As for the Me-C films of previous section compositional and structural changes result in changes of the properties. **Paper 3** investigates the change in properties at different compositions in the Nb-Si-C system. Results from the Zr-Si-C system in ref. [38] were used in order to separate between the effects of Si and choice of transition metal, in comparison to my Nb-based system. That work observed direct dependence between the relative amount of strong Si-C bonds and mechanical properties in the amorphous material [38]. In my results from the Nb-Si-C system the relation between the relative amount of Si-C bonds and the hardness of the films is confirmed, whereas the reduced elastic modulus is affected by the choice of transition metal. These are promising results since high wear resistance depend on a high H/E ratio [40] and such films therefore can be achieved by appropriate choice of film composition and transition metal.

3.4 Me-Ge-C

In sputtered Me-Ge-C films at temperatures below 400 °C the addition of Ge similar to the case of Si disturbs the growth of the Me-C leading to smaller grains [41] or even amorphization of the Me-C phase [42]. However, Ge is a weaker carbide former than Si and does not form carbides in thin films. Instead Ge agglomerates and up to 90 % of the Ge content can be bonded to Ge (**Paper 6**). The Ge can then either be in an amorphous phase as found in **Paper 6** or in an elemental crystalline phase as have been observed by X-ray diffraction for other systems [41-43].

Also, the electrical properties are affected by addition of Ge. In magnetron sputtered V-Ge-C films deposited at 300 and 400 °C a reduction of the resistivity was observed at the addition of Ge compared to the binary V-C nanocomposite, even if the cause was not totally clarified [42]. A comparison between different A-element (A = Si, Ge or Sn) in Ti-A-C-Ag coatings for electrical contact applications show that Ge gives the lowest contact resistance among the investigated coatings [41].

Nb-Ge-C is a rather unexplored material system. Spear investigated the system in the 80's by arc-melting and rapid quenching of pellets from elemental powders to determine equilibrium tie-lines between solid phases in ternary phase diagram [44]. Recently, in work related to but not included in this thesis, we predicted by theoretical calculations the stability of a previously unknown Nb₂GeC MAX-phase, which we were also able to synthesize with magnetron sputtering [45].

In **Paper 6** I investigate at the structure and electrical properties of Nb-Ge-C samples deposited with magnetron sputtering at a lower deposition temperature (200 °C).

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4 Deposition processes

There are several techniques for the deposition of thin films. Wet chemical processes such as *electroplating* use an electrolyte to transport metal ions and deposits them on a conducting surface. In *vapor deposition* the material is transported to the substrate in a gas phase. Vapor deposition can be further divided into the categories of *chemical vapor deposition* (CVD) and *physical vapor deposition* (PVD). In CVD the film growth occurs through chemical reactions introduced by the precursors in gas phase. This method is useful for complex substrate surfaces since the gas can go into cavities. However, the reactions in CVD often require high temperatures, which limit the choices of substrates. For heat-sensitive substrates PVD can instead be used. One common way of vaporizing the material in PVD is by *sputtering* where atoms in the source material are hit by ions and ejected towards the substrate [1]. The use of sputtering was reported by Grove as early as 1852 [2]. Sputtering, or more precisely a variant called *dc magnetron sputtering*, is also the technique used for all the films analyzed in thesis. Therefore, *magnetron sputtering* will be described more in detail in the following section.

4.1 Magnetron sputtering

Fig. 4.1 shows a schematic figure of the magnetron sputtering process. In the process atoms are ejected from the source (target) by ions from the plasma. The atoms then travel through the chamber (and the plasma) and some of them end up at the substrate where they can be deposited. To avoid contamination from other elements in the film, magnetron sputtering is performed at low background pressure in a vacuum chamber. A gas is introduced to the chamber to provide the ions that ejects the target-atoms. If no reactions with the gas are wanted (non-reactive sputtering) an inert gas, typically Ar (as for the films in this thesis), is used. Otherwise e.g. oxides and nitrides can be deposited by the use of O₂ and N₂ as gas, respectively. The ions are formed in a plasma[†], which is ignited when free electrons (available in the chamber due to, e.g., cosmic radiation or thermal energy) are accelerated by an applied electric field and undergoes inelastic collisions with neutral gas atoms.

[†] Although I here mainly talk about the plasma ions, the plasma in itself is a quasi-neutral gas. This means that it consists of electrons, ions, and neutrals without any net-charge. [3]

At the target, a negative potential is used to attract and accelerate the ions in the plasma. When the ion hits the target several events can occur. Some of them are illustrated in the left part of **Fig 4.1**. Firstly, secondary electrons and photons can be emitted. The secondary electrons are important because they ionize atoms in the plasma and in this way the plasma can be sustained. The ions, in turn can knock out (sputter) atoms from the target, either directly or via a cascade of collisions. How many atoms that are sputtered per incident ion is called sputter yield and is dependent on the sputtered material and the energy of the impinging ions.

Fig. 4.1 Schematic figure of the sputtering process. Atoms from the target are transported through the plasma and deposited on the substrate.

In order to increase the degree of ionization close to the target, where the ions are needed for the sputtering process, magnets are put behind the target (hence the name *magnetron* sputtering). The formed magnetic field will trap the secondary electrons and thus confine the space where most of the ions are created. The confinement of the electrons will cause an uneven sputter rate over the surface of the target where most of the sputtered atoms come from the so called *race track*. However, too much confinement of the plasma near the target can be undesirable since plasma ions also modify the growth conditions at the substrate. This problem can be solved by an unbalanced magnetron, in which the magnetic field is strengthened at the inner or outer parts of the target. Thereby more of the secondary electrons can escape from their confinement and ionize atoms further away from the target.

The sputtered atoms will travel in the direction they are ejected until they reach the chamber wall, the substrate or collide with another atom (or ion). In such collisions, the atoms will change direction. If collisions occurs often enough the motion of the atoms will become random. These atoms are called thermalized. The average distance an atom can travel before a collision is called the *mean free path*, λ [4]. At an Ar pressure of 0.4-0.5 Pa, which is used as working pressure for the sputter depositions in this thesis, λ is roughly a couple of centimeters with longer mean free paths for the lighter elements.

An atom that lands on the substrate surface it is called adatom. The *sticking coefficient* is the probability that the atom will stay on the surface. If the adatom has some energy it can move around on the surface. The adatom mobility can be manipulated with bombardment of energetic particles. This can be achieved by applying a negative bias voltage, which attracts the ions in the plasma. The ion bombardment can increase the nucleation rate and the film density, but also the stress state in the film [5]. If too high bias is applied to the substrate, the plasma ions will start to resputter the material of the substrate.

With magnetron sputtering it is possible to deposit a wide range of materials from metals to insulators. For deposition of thin films consisting of more than one element, composite targets are available and these are often used in industrial processes where the wanted composition is known. However, when investigating how different compositions cause structural changes like in **Paper 1-3** and **6**, the use of several elemental targets will give a larger possibility to control the composition. Elemental targets were therefore used for the deposition of all films in this thesis.

The text above describes how the sputtering is caused by ions accelerated by a negative potential. There are several different techniques to do this. For the films in this thesis, a constant voltage was applied (*dc magnetron sputtering*). This technique can not be used for target materials with a resistivity larger than $10^6 \Omega\text{-cm}$ [1]. For these material, an ac or radio frequency (rf) voltage need to be applied (*ac or rf magnetron sputtering*). The high frequency will lower the impedance of the material and allow a current to pass. Since the electrons follow the changes in the electric field much faster than the ions, the target will become self-biased to a negative potential. In this way the sputtering process can go on in the same way as for a dc target with positive ions that sputter away target atoms. *Pulsed magnetron sputtering* can be used if arcing is a problem in the system. By inverting the voltage in a pulse the electrons in the plasma can discharge the target to prevent large charges from building up.

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5 Characterization

A large number of techniques are needed to analyze the microstructure and properties of thin films. In this chapter some of the techniques used in this thesis are described. The first is *transmission electron microscopy*, integrated with *energy-dispersive X-ray spectroscopy* (EDX). TEM/EDX is used in **Paper 1-6** to observe the structure and elemental distribution of the materials. Also *scanning electron microscopy* (SEM), which is another electron microscopy technique used in (**Paper 1** and **6**) is briefly described. Next, different methods using *X-ray diffraction* are discussed. These methods include θ - 2θ (**Paper 2** and **6**) and *grazing incidence* (**Paper 1** and **3**) *X-ray diffraction*, which are used for identifying the crystalline phases and texture of the materials. They also include *pole figures* and the $\sin^2\psi$ -method (**Paper 2**), which are used to determine the epitaxy and measure stress, respectively. With a low angle of incidence the X-rays will be reflected rather than diffracted. *X-ray reflectivity* can be used to determine the density of a material (**Paper 6**). *X-ray photoelectron spectroscopy* (XPS) is used to determine the composition (**Paper 1-6**) and describe the bonds between the atoms (**Paper 1-3** and **6**) is described. Finally methods for characterization of the electrical properties *resistivity* (**Paper 1, 3, and 6**) and *contact resistance* (**Paper 1** and **6**) are described.

5.1 Transmission electron microscopy (TEM)

One of the more important techniques considering the work in this thesis is transmission electron microscopy. It is a powerful technique since it combines high spatial resolution with crystal information from electron diffraction. In **Papers 1-3** and **6** it is used to help determine the structural evolution of the studied materials on the nano-scale. TEM can also be combined with other analytic methods to get information about the distribution and composition of the elements in the film. One example is EDX, which is used in **Paper 2** in order to show segregation of Si. In the TEM, electrons are emitted from an electron gun and accelerated by a high voltage. For the material science of transition metal carbide based materials, the acceleration voltage typically lies between ~100-300 kV. An advanced set-up of magnetic lenses is then used to focus and direct the beam through the microscope and form an image of the sample. This section will describe how an image or diffraction pattern is formed and used after a beam with parallel electrons has interacted with the sample, followed by descriptions of EDX and sample preparation. A discussion about electron-beam-induced crystallization during high resolution TEM studies (**Paper 4 and 5**) is presented in **Ch. 6**.

5.1.1 Imaging

Since the wavelength of the electrons at 200 keV is very short (2.5 pm), the theoretical resolution of the microscope is as high as 0.02 Å. In practice, due to instrumental and atomic aberrations, the best spatial resolution is not that high, but is still enough for atomic resolution.

Fig. 5.1 shows a simplified model of the electron path through the sample and down to a fluorescent screen or CCD-camera. **Fig. 5.1a)** shows the imaging system, which consists of three lenses. The *objective lens* forms the first image of the sample. The corrections of this lens are important since all imaging errors made by the lens will be magnified by the other lenses in the system. The second lens is called the *intermediate lens*. By changing the lens current for the intermediate lens the operator can switch between diffraction and imaging simply by pressing a button. The last lens, the *projector lens*, magnifies the image or diffraction pattern of the sample even further.

Fig. 5.1 a) simplified model of the electron path through the imaging lenses, b) projection of the image in the objective lens, c) selected area electron diffraction, and d) real space micrograph.

Fig. 5.1b) shows the projection in the objective lens. As the electrons go through the sample they can interact with material in several different ways. Some of them are transmitted without any change (solid lines), while others are scattered by the atoms in the sample (dashed lines). All the electrons scattered in one direction will come together in a point in the back focal plane, i.e., point X for the direct beam and point Y for the scattered electrons in the figure. All the points together make up the electron diffraction pattern. The electron path can thereafter be further extended to the image plane where an image of the sample is formed.

An example of an electron diffraction pattern (Ti-Si-C sample, **Paper 2**) is shown in **Fig. 5.1c)**. The image of the diffraction pattern is formed by placing the object plane of the intermediate lens in the back focal plane of the objective lens. The pattern in the figure consists of circles which are more intense in some of the areas.

The black triangular shape is a beam blocker, which is used to protect the CCD-camera from the high intensity of the directly transmitted beam. From the pattern we can obtain information about the lattice spacings (radii of the circles), crystal structure (distribution of the circles), and crystal orientation. A circle with homogenous intensity indicates a polycrystalline structure with randomly oriented crystallites. In the viewed sample there is, however, some ordering (a (111) preferred direction) among the crystallites and therefore the third circle from the center has higher intensity in some directions (the {220} spots). In this way more and more order will finally give rise to a dot pattern when the intensities from the rings are concentrated in specific directions or vanish depending on the orientation of the grains. Amorphous material (studied in **Paper 3-5**) will scatter equally in all direction and therefore only form very diffuse circles. There is often a wish to have diffraction patterns from only one part of the prepared sample (e.g., excluding the substrate). This can be done by inserting an aperture (*selected area aperture*) in the image plane of the objective lens. The area of the image where the beam then can pass is the same as from which the viewed diffraction pattern originates.

The real space image corresponding to **Fig. 5.1c**) is shown in **Fig. 5.1d**). The image is formed by placing the object plane of the intermediate lens in the image plane of the objective lens. The scattered electrons are important for imaging since they are the origin of most of the image contrast. The image contrast can be increased by inserting an aperture (*objective area aperture*) in the back focal plane of the objective lens. If the electrons in point Y (**Fig. 5.1b**)) are blocked, regions scattering more in this direction will appear darker since these electrons do not contribute to the image anymore. If the transmitted beam (point X) is screened by the objective aperture, all the image contrast is made up of scattered electrons. All regions not scattering electrons (e.g., a hole in the sample) will appear totally black and this technique is therefore called dark field imaging. The technique can be useful for identifying crystal grains with a certain orientation, by selecting this orientation with the objective area aperture in the diffraction mode. These grains will then appear bright in imaging.

Thus, atomic resolution together with the ability to easily record diffraction patterns is one of the big advantages of TEM since it is possible to obtain both real and reciprocal space information from a specifically selected part of the sample. The microscope can also be equipped with other instruments such as EDX (see **Section 5.1.2**) or EELS to be able to obtain compositional information.

There are also some drawbacks with TEM. One disadvantage is that the sample has to be electron transparent (i.e. <100 nm for most materials). This means an extensive sample preparation (See **Section. 5.1.3**), which in worst case might affect the composition. The sample preparation usually gives only a very small volume from each sample that can be imaged. The investigated volume then has to be assumed representative for the whole film. Care should also be taken not to misinterpret features, e.g., overlapping grains when the three-dimensional volume of the sample is projected into a two-dimensional image.

5.1.2 Energy-dispersive X-ray Spectroscopy (EDX)

As mentioned earlier, TEM can be implemented together with other instruments. In EDX (also called EDS), the energy of emitted X-rays from the sample is analyzed. This is possible because atomic electrons in the sample can be excited by the beam. After one excitation, an electron from a shell further out will take the place of the excited electron in order to lower the total energy of the atom and at the same time an X-ray photon is emitted. The energies of the emitted photons are characteristic for each element and can therefore be used to identify the elements [1]. As an example, the EDX spectrum from a Ti-Si-C sample is shown in **Fig. 5.2**. In the spectrum the peaks of the elements in the film is seen.[†] The intensity of the different peaks depends on composition, but also on the type element, the thickness of the sample and the crystallographic orientation of crystallites in the sample. Sensitivity factors can be used in quantitative analysis, but care should be taken especially for the lighter elements (in this case C), which are difficult to quantify.

Fig. 5.2 a) example of EDX spectrum from a Ti-Si-C sample. b) STEM micrograph from the same Ti-Si-C sample with EDX map of Ti and Si from the marked region inserted.

A special variant of TEM often used in connection with EDX is *scanning transmission electron microscopy* (STEM). In STEM the beam is focused to a small spot and the image is formed by continuous scanning over an area. The advantage of this is that an EDX spectrum can be acquired from a very small region. The use is shown in **Fig. 5.2b**), where elemental mapping of Si and Ti (insets) have been performed. The maps are created by acquiring one EDX spectrum for each point in the marked region. In each spectrum the intensity of the Ti_{Kα} and Si_{Kα} peak is integrated and plotted in the Ti and Si map, respectively. This example comes from **Paper 2**, and shows how Si has segregated from the TiC structure out to the grain boundaries.

[†] In addition also a small Al peak just below the Si peak can be seen. This peak probably originates from material coming from the Al₂O₃ substrate.

5.1.3 Sample preparation

Depending on the cutting different information can be obtained as illustrated in **Fig. 5.3**. The sample in the figure has a columnar structure, which is seen for several samples in this thesis. If a cross-sectional specimen (cut A) is prepared the growth evolution can be studied. This is useful for example for showing how the thickness of the initial epitaxial layer changes with Si content in **Paper 2**. However since the columns have small diameters they will overlap and elemental mapping of the phase between the columns is hard to achieve. In **Paper 2** this problem is solved by instead using a plan-view sample (cut B in **Fig 5.3**). The columns are now viewed along their elongated axis so that the projected image will have a minimum of overlapping columns. Thereby, the segregation of Si out of the columns could be mapped by EDX.

Fig. 5.3 Schematic of a columnar structure with A and B marking the ways of cutting the sample into a cross-section and a plan-view, respectively. Growth direction is marked in the figures.

Independent of the choice of cutting the sample needs to be thin enough to be able to transmit electrons through the material. For most material, this means a specimen thickness of less than 100 nm.

There are several ways to prepare electron-transparent specimens. Most of the TEM images presented in this thesis are from cross-sectional specimens where the film was cut and glued into a grid with two film sides facing each other. The specimens were then mechanically polished down to a thickness of $\sim 50\text{ }\mu\text{m}$ and a surface roughness of $\sim 1\text{ }\mu\text{m}$ before they were put in an ion miller. In the ion miller the specimens were thinned further by Ar^+ ions with energy of 5 keV to achieve electron transparency. In a final step the energy of the Ar^+ ions is reduced to 2 keV for 10 min in order to remove sputter-induced residuals from the surface.

Also plan-view specimens are used. These are prepared from a circular disk of the sample, which is cut and polished from the substrate side. In order to avoid the supporting substrate from cracking during the process, only the center of the disk is thinned to a thickness of $\sim 50\text{ }\mu\text{m}$, with the help of dimpling, while the rest of the specimen is left with a thickness $\sim 100\text{ }\mu\text{m}$. The specimen is then ion-milled to electron transparency in the center. If the specimen is ion-milled only from the substrate side, voided regions between the columns can be observed. Therefore,

the specimen is also ion-milled from the top. One difficulty with this is to know how far up in the film the specimen is viewed and several iterations going between the ion-miller and TEM can be necessary.

An important aspect is how the sample preparation affects the structure and chemical composition of the material. It is, for example, shown that the clean-sputtering with Ar^+ ions prior XPS measurements changes the binding structure of metastable Ti-Me-C (Me=Al, Fe, Cu or Pt) already at low ion energies (<4 keV) [2]. This is in the same range as the Ar^+ energy used for the ion milling in TEM sample preparation and the question of ion induced damage in the samples are thus motivated. In **Paper 4 I** therefore compare Nb-Si-C TEM specimens prepared by ion milling, and specimens prepared by the *small angle cleavage technique* (SACT) [3]. In SACT, the sample is cleaved in such way that cross sectional electron transparent regions are formed. Therefore, no ion milling is necessary for this method. However, often only a very small region will be electron transparent [4]. In the case of Nb-Si-C only modest differences were seen between the two methods and the conclusion was that the ion milling did not have any distinguishable effect on these samples.

5.2 Scanning electron microscope (SEM)

Like TEM, SEM detects electrons to form an image. The acceleration voltage is, however, much lower (typically 5-30 keV). This gives a lower resolution than TEM (although still much higher than an optical microscope), but is much easier to use since it needs little or no sample preparation if the sample is conductive, vacuum compatible and unaffected by the electron beam.

SEM uses a scanning electron beam that is moving over the surface of the sample. The primary electrons from the beam interact with the material and the electrons emerging out from the sample is detected in order to form an image of the sample. Detection of secondary electrons emitted from the outer electron shells will give a topographical contrast in the image. Since these electrons have low energy (<50 eV) they will come from a confined place close to the surface. There are also electrons that are elastically backscattered by the atom nuclei. Heavier atoms will backscatter more and therefore a compositional contrast can be imaged. However, this will not give information of which elements there are in the film. For identification and quantification of elements SEM is often combined with an EDX detector.

5.3 X-ray diffraction (XRD)

XRD is extensively used in material science since it is both easy to use and nondestructive. In XRD, X-rays are radiated onto a material. The X-rays will interact with the material and information about the crystal structure can be obtained from the diffracted X-rays.

5.3.1 Bragg's law

The reason to use X-rays is that their small wavelength, λ , (1.54 Å for Cu_{Kα}) is comparable to the distance between the atoms in materials, i.e., X-rays can resolve the atomic plane spacing. The X-rays diffract with constructive interference according to Bragg's law

$$n\lambda = 2d_{hkl}\sin(\theta), \quad (5.1)$$

where n is an integer, d_{hkl} the plane distance between two planes with index hkl , and θ the scattering angle. Not all combinations of hkl will give a diffraction peak. The allowed reflections are given by the structure factor, which can be calculated from the crystal structure. [5] The peak positions are dependent on which atoms are present in the structure. Thereby each material will have its own “fingerprint” from which it can be identified using XRD.

Fig. 5.4 Notation of angles used in XRD.

The X-ray peaks can only be detected if the condition in **Eq. 5.1** is fulfilled, which implies that the material is crystalline with large enough grains. If the grain size is reduced this is observed as a drop in peak intensity and a peak broadening can also be seen when. The peak broadening can be used to calculate the grain size by using the Scherrer's formula [6]. (**Paper 1, 3, and 6**). When the grain size becomes smaller than 2-5 nm it is no longer possible to see any reflections. The material is then called X-ray amorphous.

5.3.2 Different X-ray diffraction methods used

In order to find the planes that fulfill Bragg's law and in which direction they are oriented, both the incident X-rays and detector as well as the sample orientation need to be varied. The notations of the varied angles in this thesis are illustrated in

Several different methods to vary these angles in order to find constructive interference are available. The three of them used in this thesis are illustrated in **Fig. 5.5**. These are a) θ - 2θ , b) *grazing incidence X-ray diffraction (GIXRD)*, and c)

pole figures. In the figures an epitaxial (A) and a poly-crystalline (B) film of Ti-Si-C (**Paper 2**) are shown.

Fig. 5.5 Epitaxial TiC_x (A) and polycrystalline Ti-Si-C (B), viewed with different X-ray techniques. a) θ - 2θ , b) GIXRD, and c) pole figure of TiC 200.

In a θ - 2θ measurement (illustrated by **Fig. 5.5a**)) the angle of incident and reflected beams are changed simultaneously and always kept equal to each other. This means that only crystal planes parallel to the surface will contribute to the diffraction pattern. Film A, which has all the (111) planes oriented this way, therefore shows much stronger peaks than B in which the planes are more randomly oriented and the crystallites are smaller.

GIXRD (**Fig. 5.5b**)) instead uses an incident beam at a small constant angle, ω , and varies the outgoing angle, 2θ . This means that the planes fulfilling Bragg's diffraction condition in general are not parallel to the surface. GIXRD is therefore useful when having non-textured materials with grains randomly oriented like film B. For the substrate and film A, the Bragg condition is never fulfilled and therefore no peaks can be seen.

In a pole figure (**Fig. 5.5c**)) the outgoing beam and the detector are fixed at one chosen θ - 2θ value, i.e., at one specific plane distance. The sample is then rotated in the ψ and Φ directions and the detected intensity can be plotted onto a

stereographic projection. If the sample is highly textured, as for A, the Bragg condition will only be fulfilled in certain directions and peaks will be seen in the pole figure. If we instead have a sample with grains more randomly distributed in the film the pole intensity will decrease, as for B. In **Fig. 5.5c** the θ - 2θ value was set to correspond to d_{200} for TiC. This value coincides with the d_{0006} value of the $\text{Al}_2\text{O}_3(0001)$ substrate peak and therefore an intense peak can be seen at the center of both pole figures.

5.3.3 Strain measurements ($\sin^2\psi$ -method)

In **Paper 2** a shift of the 111-peak was seen with increasing Si content. In order to exclude the possibility that this shift was due to strain the $\sin^2\psi$ -method was used. The accuracy of this method should not be overestimated, but the technique gives an estimate of the in-plane stress, σ and allows for calculation of the strain free lattice parameter a_0 . [7]

Fig. 5.6 Measurements of the lattice parameter vs. $\sin^2\psi$, and stereographic projection with the measured crystal-directions (filled symbols).

A tensile stress in a thin film will cause an expansion of the lattice planes in the direction normal to the surface. At the same time a compression will be seen of the planes parallel to the surface. The expansion and compression is coupled by the Poisson ratio, ν . In the $\sin^2\psi$ -method this change is often observed by measuring the plane distance for a certain plain, d_{hkl} , at different ψ . However, if the stress is measured on an epitaxial film (**Paper 2**) different d_{hkl} must be chosen for different directions of ψ . In this case the lattice parameter a , rather than a selected plane spacing is used in the plot against $\sin^2\psi$.

One example of a stress measurement is shown in **Fig. 5.6**. The data points are marked with the indexes of the d_{hkl} from which a was calculated. The positions of the poles are marked with the symbols from plot, in the stereographic projection (inset **Fig. 5.6**). The open circles in the inset show other directions from which a can be measured in the crystal. The figure shows that a linear curve (solid line) can be fitted to the data points. The curve has the equation

$$a = m \sin^2 \psi + k , \quad (5.2)$$

where m and k are constants.

For a stress independent of the azimuth angle Φ , the following equation can be derived (see [7] for a more detailed derivation).

$$\varepsilon = \frac{1+\nu}{E} \sigma \sin^2 \psi - \frac{2\nu}{E} \sigma . \quad (5.3)$$

Also knowing that the stress can be expressed as the relative change in a from the strain free lattice parameter it is possible to combine **Eq. 5.2** and **5.3**.

$$\frac{1+\nu}{E} \sigma \sin^2 \psi - \frac{2\nu}{E} \sigma = \varepsilon = \frac{a-a_0}{a_0} = \frac{m}{a_0} \sin^2 \psi - \frac{k-a_0}{a_0} . \quad (5.4)$$

Identifying the term in front of the $\sin^2 \psi$ term gives the stress

$$\frac{1+\nu}{E} \sigma = \frac{m}{a_0} \Leftrightarrow \sigma = \frac{mE}{(1+\nu)a_0} . \quad (5.5)$$

If a_0 is not known this can be calculated from the **Eq. 5.2** by first putting $\varepsilon=0$ in **Eq. 5.3**, which gives a value for the strain-free direction ψ^* .

$$\varepsilon = 0 \Rightarrow 0 = \frac{1+\nu}{E} \sigma \sin^2 \psi^* - \frac{2\nu}{E} \sigma \Leftrightarrow \sin^2 \psi^* = \frac{2\nu}{1+\nu} . \quad (5.6)$$

The value for $\sin^2 \psi^*$ can then be used in **Eq. 5.2** to calculate a_0 . From the equations it is clear that the $\sin^2 \psi$ -method assumes that the Poisson ratio for the material is known. In the example in **Fig. 5.6**, the value 0.19 [8] (TiC) is used which gives $\sin^2 \psi^*=0.32$. Both $\sin^2 \psi^*$ and the corresponding a_0 have been marked in the figure.

5.3.4 X-ray reflectivity (XRR)

If a θ - 2θ measurement is carried out at very low angle ($2\theta < 4^\circ$) it is instead referred to as X-ray reflectivity (XRR). Below a certain angle, called the critical angle, all the X-rays will be totally reflected by the film. At the critical angle the intensity drops dramatically as shown in **Fig. 5.7a**). The 2θ -value for the critical angle depends on the refractive index of the film. Since the refractive index is a

function of the electron density the density of the film can be calculated from the critical angle if the composition of the film is known. As an example film B in **Fig. 5.7a)** has a higher critical angle than film A and therefore, film A has a higher electron density. This was used in **Paper 6**, where the density calculated from XRR was compared with a theoretically calculated density. In this way it could be shown that the films were porous with a correlation between the porosity, the oxygen content and the resistivity of the films.

Fig. 5.7 XRR measurements for a) density b) thickness.

For thin films, typically less than 100 nm thick, constructive interference between the substrate surface and the film surface will at low angles give rise to so called Kiessig fringes as shown in **Fig. 5.7b)**. The shape of the fringes and the distance between them depend on the film thickness and the surface roughness. These two properties can therefore be modeled from the data. In this work, the modeled thickness has been used for calculating the growth rates of the films.

5.4 X-ray photoelectron spectroscopy (XPS)

In XPS or ESCA (*Electron Spectroscopy for Chemical Analysis*) X-ray photons are used to eject electrons from the core levels of the analyzed material. Since both the photon energy (E_p) and the work function (W) are known the detected kinetic energy of the emitted electrons (E_k) can be used to calculate the binding energy (E_b).

$$E_b = E_p - E_k - W. \quad (5.7)$$

The binding energy is characteristic for each material and by plotting E_b against the intensity a qualitative analysis of the composition can be done. For a quantitative analysis the area of each peak must be calibrated using elemental specific sensitivity factors. The sensitivity factors can be obtained by XPS measurements on samples with known composition. In this thesis the composition of selected sets of samples were therefore also measured by Elastic Recoil Detection Analysis (ERDA) or Rutherford Backscattering Spectrometry (RBS)

The orbital from which the electrons are emitted will be affected by neighboring atoms. This is seen as a small chemical shift of the peak and thereby different bonds in the material can be detected.

Even if the X-rays penetrate deep into the material, the escape depth of the photoelectrons is usually less than 10 nm, which makes XPS a surface sensitive method. For analysis deeper down into the material, sputtering is often used to remove the top surface.

5.5 Electrical resistivity

Fig. 5.8 Schematic of a four point probe measurement setup

A four point probe instrument has been used to measure resistivity. To avoid substrate effects, the thin films for this purpose were deposited onto isolating substrate material (SiO_2). An illustration of the setup is shown in **Fig. 5.8**. During the measurement the four probes sitting in a line at equal distances are pressed against the material. A current is applied between the outer probes and the voltage between the two inner probes is measured. Since there is no current going through the inner probes there is no contact resistance influencing the measurement. In the case of thin films where the thickness of the film, t_f , is much smaller than the distance between the contacts, a , and an infinite surface the expansion of the current can be assumed to be cylindrical around the conducting probes. The cross-sectional area, A_c , at a radial distance r from a probe through which current flows is then given by

$$A_c = 2\pi r t_f. \quad (5.8)$$

Since the voltage is measured between the inner probes an expression for the resistance, R , in the material is given by

$$R = 2 \int_a^{2a} \frac{\rho dr}{2\pi r t_f} = \frac{\rho \ln(2)}{\pi t_f}. \quad (5.9)$$

In **Eq. 5.9**, ρ is the resistivity to be calculated. Rewriting **Eq. 5.9** and applying Ohm's law gives

$$\rho = \frac{\pi t_f}{\ln(2)} R = \frac{\pi t_f}{\ln(2)} \frac{U}{I} \approx 4.532 t_f \frac{U}{I}. \quad (5.10)$$

U and I are measured in the four-point probe setup, while the thickness of the film must be obtained with some other method. In this thesis this was done using cross-sectional SEM. To correct for the finite sample size the obtained resistivity must be multiplied by a factor, which with a sample size of (10x10 mm) and the probe used ($a = 0.5$ mm) is 0.9822.

5.6 Electrical contact resistance

The contact resistance is an important property for all contacts. In an application the contact resistance should be both low and stable over time. There are different setups for measuring the contact resistance. In **Paper 1** a crossed-cylinder geometry, as shown in **Fig. 5.9a**), was used. In this setup two Ni-plated Cu cylinders (20 mm length, 10 mm diameter) is used. One cylinder is coated with Ag the other with the contact material of interest. At the same time as a force is applied a current is sent through the cylinders as shown in the figure. By measuring the voltage and the current, the contact resistance can be calculated by Ohm's law.

Fig. 5.9 Contact resistance measurement setup with a) crossed cylinders and b) a four-terminal measurement.

In the cross-cylinder setup the contact force is typically measured above 50 N. To come closer to simulate a low contact force application a four-terminal measurement, as shown in **Fig. 5.9b**), was instead used to measure the contact resistance between 0-10 N in **Paper 6**. In this setup the film is placed on a fixed support. When the upper part is lowered the spring supported terminals U^- and I^- will contact first. These two terminals are isolated from the rest of the upper part. When the gold probe (diameter 4.42 mm) is in contact with the film a dc current (I) goes from I^+ through the probe to I^- . The contact resistance is calculated by Ohm's law as for the crossed cylinders by regulating the current and at the same time measuring the voltage between U^- and U^+ . The inner resistance of the gold probe is constant and low and can therefore be ignored. Also the leakage current (I_L) from the probe to U^- is negligible compared to the current from I^- to I^+ .

As described in **Ch. 2**, the contact resistance is mainly caused by the constriction resistance. Therefore the contact resistance is not only a property of the contact material, but also of the application (e.g., force applied), used substrate and

surface contamination. As example Ag deposited on Ni-plated Cu shows a contact resistance of 1.2 m Ω at 10 N and a probe size of 4.42 mm, while Ag on steel shows a contact resistance of 3 m Ω measured under the same conditions. If the probe size is changed to 1.2 mm the Ag on steel will show a contact resistance of 3 m Ω already at 1 N. In this thesis an Ag reference thin film deposited on the same kind of substrate is therefore always used as comparison.

Fig. 5.10 Contact resistance as a function of contact force.

The contact resistance is often plotted as a function of the contact force. A typical behavior of the contact resistance for the films investigated in this thesis is shown in **Fig. 5.10**. At low contact forces an isolating oxide layer makes the electrical contact area small and the contact resistance high. As the force increases the oxide breaks and there is a rapid decrease in contact resistance. Since the oxide is no longer present and possible also due to plastic deformation of the probe and film, the unload curve will have a lower contact resistance.

5.7 Nanoindentation

Nanoindentation is a common way of evaluating the hardness and elastic modulus of thin films. In this technique a diamond tip is pressed into the material resulting in load-displacement curves as the example showed in **Fig. 5.11**. For the measurements done in these thesis these curves was evaluated according to the Oliver-Pharr method [9]. Then the reduced modulus, E_r , is given by

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A}} \left(\frac{dF}{dh} \right), \quad (5.11)$$

in which A is the contact area of the tip, and (dF/dh) the contact stiffness of the material. The contact stiffness is determined from the first part of the unloading curve as showed in **Fig. 5.11**. If the Poisson's ratio (ν) of the material is known the elastic modulus, E , of the material can be calculated by inserting ν together with the Poisson's ratio (ν_t) and elastic modulus (E_t) of the tip in the equation

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_t^2}{E_t}. \quad (5.12)$$

The hardness (H) is calculated from the contact area and the maximum load F_{max}

$$H = \frac{F_{max}}{A}. \quad (5.13)$$

Nanoindentation measurements on thin films can easily be influenced by substrate effects if the indentation depth is too large. To avoid this, the maximum load used for the measurements in this thesis was calibrated so the maximum displacement did not exceed 10 % of the total thickness of the film.

Fig 5.11 Typical load-displacement curve observed under nanoindentation

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6 Electron-beam-induced crystallization

In **Papers 4** and **5**, electron radiation effects on Me-Si-C (Me = Nb or Zr) are investigated. In both cases crystallization of the amorphous phase in the material was found to occur during electron microscopy analysis. This chapter describes the different processes that were considered as possible causes for the crystallization followed by some comments on how these materials could be studied without microscopy-induced artifacts.

6.1 Radiation damage processes

There are several ways in which electron radiation can cause structural and chemical changes to the sample [1-3]. In order to determine the cause of the crystallization observed in the amorphous Me-Si-C, the following radiation effects were considered.

Fig. 6.1 The maximum transferable energy for materials used in this thesis as a function of the energy of the electrons in the electron beam. (The energies are calculated using Eq. 2 in [3])

6.1.1 Atomic displacement (“knock-on”)

Elastic scattering process can cause damage to the sample by a “knock-on” process between a nucleus in the sample material and the incident electron. The amount of energy that can be transferred (E_T) will be dependent on the incident

angle of the electron, the atomic mass, and the energy of the electron. **Fig. 6.1** shows the maximum value for E_T when an electron hits the nucleus straight on and then backscatters. As can be seen, more energy is transferred for light elements and for higher incident electron energies. If E_T is larger than the displacement energy E_d , the atom will be moved from its position as shown in **Fig. 6.2**. If this happens in a crystal (**Fig. 6.2a**) a Frenkel defect consisting of a vacancy and an interstitial can be created. For a high defect density, the material may undergo amorphization. In an amorphous phase (**Fig. 6.2b**), atomic displacement can cause density fluctuation in form of a free volume and an anti-free volume. These density fluctuations may in turn crystallize the material [4].

Fig. 6.2 Displacement of atoms may lead to a) creation of Frenkel defects in a crystal, b) density fluctuations in amorphous materials. (Figure reproduced from [5].)

If the atom hit by the electron is positioned at the surface of the material, the atom can leave the material instead of being displaced. This process is called electron sputtering and the required energy E_s is usually much lower than E_d . Since the electron hitting the atom will be traveling through the sample, sputtering is more likely to occur on the back-side of the specimen.

Element	E_T [eV]	E_d [eV]	E_s [eV]
Ti	10.9 ^b	15 ^a	4-8 ^a
Nb	5.64 ^b	24 ^a	6-12 ^a
C	43.7 ^b		
Si	18.7 ^b		
Zr	5.74 ^b		

Table 6.1 Some data for the pure elements. E_T is the maximum transferable energy at 200 keV, E_d is the displacement energy and E_s is the sputtering energy.

^a From Table 4.3 in [1]

^b Calculated from eq. 2 in [3]

Table 6.1 shows the values of for the maximum transferable energy to the discussed elements using incident beam electrons with the energy of 200 keV. Shown are also the displacement and sputter energies for some of the elements in their pure form. It should be noted that E_d and E_s are not strictly valid for the

investigated materials in this thesis since the chemical environment in an amorphous compound is different compared to the pure elemental states. The values should instead be seen as reasonable estimates.

Displacement and sputter damages are the most common radiation damages seen in metals and the only way to avoid them is to lower the incident electron energy so that the maximum transferable energy does not exceed the displacement energy. In **Paper 4** this effect is clearly seen, as the crystallization process is significantly slower if the energy of the beam electrons are lowered from 200 to 80 keV. If it is not possible to lower the electron energy below the displacement energy, the electron dose should be minimized for the required resolution in order to reduce damages.

6.1.2 Specimen heating

Specimen heating is caused mainly by phonon vibrations in the material. The main parameters that affect the specimen heating are the beam current and the thermal conductivity of the material. This is shown in **Fig. 6.3**, where materials with different thermal conductivity κ (in W/mK) from insulators ($\kappa=0.1$) to good thermal conductors ($\kappa=100$) like metals are represented. In **Fig. 6.3**, the grey region marks the beam current as measured in the TEM used for the main part of the experiments in this thesis. As can be seen from the figure, beam heating should not be a big problem for these currents. However, if a small particle with good thermal conduction is embedded in a matrix of material with lower thermal conductivity, the heating of the particle can be considerable.

Fig. 6.3 Specimen heating as a function of beam current. The lines marks materials with different thermal conductivity, κ (W/mK). The gray region marks the beam current as measured experimentally for the TEM used in this thesis. (Figure reproduced from [1].)

Even if the heating is small it may be enough to increase the diffusivity of particles in the material and thereby induce changes in the structure. Nagase and

Umakoshi [5] have, for example, shown that electron beam induced crystallization shows significant temperature dependence by using MeV electron irradiation on Fe-Zr-B samples at room temperature and below. The best way to avoid heating is by cooling of the sample. This is done using such a sample holder in the TEM.

6.1.3 Radiolysis

The chemistry and structure of covalent and ionic materials can be changed by radiolysis. In this process an inelastic scattered electron excites an electron in the material to make an interband transition. It is then possible for the electrons and holes to recombine and form an anion vacancy and a cation interstitial. The best way to reduce radiolysis is to decrease the initial electron-electron interaction. This can be achieved by having thinner samples or higher acceleration voltage.

6.2 Viewing non-stable samples

I have experienced several difficulties in performing the experiments that lead to the conclusions drawn in **Paper 4** and **5**. First was the problem with viewing the samples in their as-deposited state and later to follow the crystallization process. In this section I describe my solutions to these problems.

6.2.1 The as-deposited state

It is of great importance to correctly image the true structure of materials in TEM since conclusions about material properties often are related to the microstructure. Although a material can look amorphous in XRD, high resolution TEM images can sometimes reveal small nanosized grains. In order to acquire these images, focus and astigmatism have to be corrected, which demands adjustments when viewing the specimen. For beam-sensitive samples, this is difficult since their structure is changed due to the beam. Especially difficult in my studies were the Nb-Si-C samples, which showed signs of crystallization within a few minutes at normal imaging conditions.

The solution I used to correctly image the specimens was a so called low-dose technique. Here, the adjustments are made in one area of the specimen and then, after moving to another location, an image is quickly acquired before a critical dose starts the crystallization. The movement of the sample often changes the viewing conditions and therefore this technique usually involves some trial-and-error before a good image can be obtained.

6.2.2 Observing crystallization

To make observations of the crystallization process and compare different samples, the electron dose of the specimen should be known. This can be calculated through the beam current, the exposure time, and the irradiated area.

The beam current should ideally be measured at the position of the sample by trapping all incoming beam-electrons in a Faraday cup. An alternative way, which I have used, is to measure the current coming down to the fluorescent viewing plate. This can be done with the unobstructed beam through a hole in the specimen in connection with the experiment and in this way a regular TEM-sample holder can be used.

During the observation the exposure time was measured. In several of the observations the image had to be corrected for drift of the specimen. This was done manually by tracking the sample continuously.

Fig. 6.4 Process for determining the structure and phase of the crystallized material. In the lower row an ABSF filter have been applied to remove background noise from the amorphous phase.

The irradiated area was kept constant to a diameter of ~ 100 nm in all experiments. These areas are too small for proper viewing by electron diffraction in a useful way to determine the phases and instead the fast Fourier transforms (FFT) of HRTEM images was used. As an example the FFT for a $\text{Zr}_{.53}\text{Si}_{.20}\text{C}_{.27}$ sample (**Paper 5**) is shown in **Fig. 6.4 a)**. In the upper row of this figure, the regular FFT is shown. In the lower row an average background subtraction filter (ABSF) have been applied to remove some of the remaining amorphous component. A description of this filter can be found elsewhere [6]. Rather than measuring the reciprocal distance to all observed grains in the FFT, a rotational average was calculated which gives the radial intensity distribution from the center of the FFT as shown in **Fig. 6.4 b)**. The scales in b) are not calibrated. I used an FFT from the single crystal Si substrate taken at the same time as the other FFTs to calibrate the scale and after removing the background the result is presented in **Fig. 6.4 c)**. In this way I show that the best match is an fcc structure with an lattice spacing of $4.58 \text{ \AA}$, which among the possible candidates fits best to the NaCl (B1) structure of ZrC_x .

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7 Summary and contribution to the field

This thesis concerns the microstructure of transition metal carbide based thin film materials. This is a large class of materials with interesting properties for both electrical and mechanical applications. The properties depend to large extent on the microstructure and the ability of tailoring the structure by appropriate choice of composition with different alloying elements makes it an interesting field to study. For industrially relevant substrates, the deposition temperature is usually kept low (<400 °C). One way to do this is to use magnetron sputtering. However, the evolution of film properties and structure can be rather complex for both binary and ternary systems, when deposited at temperatures far from thermal equilibrium. *My work has therefore been to increase the knowledge of the structure and properties of transition metal carbide nanocomposites when deposited with magnetron sputtering at these relatively low deposition temperatures.*

7.1 Nb-C as electrical contact material

For electrical contact applications, Ti-C based nanocomposites with addition of, e.g., Si have attracted attention with promising results [1-5]. However, both Ti and Si form insulating oxides, which can cause problems for low contact force applications. Preliminary results from Lewin indicate also the Nb-C system to be a good candidate as electrical contact material [6]. In **Paper 1**, I therefore investigate the Nb-C system more thoroughly with a focus on relating the structure to electrical and mechanical properties.

This is done by depositing Nb-C thin films with unbalanced magnetron sputtering from two elemental targets using a substrate bias of -50 V and a substrate temperature of 300 °C. The result is a nanocomposite consisting of crystalline NbC grains surrounded by a matrix of amorphous C. XRD shows that the NbC grains are of the B1 (NaCl) structure. With increased C content (from 43 to 64 at.% C), TEM shows a change from grains elongated (~75 nm) in the growth direction to small (3-5 nm) equiaxed grains.

By comparing the areas of the C-C and Nb-C peaks in the C1s spectra the relative amount of amorphous carbon can be calculated from the XPS data. Although an

increase of amorphous C with increased C content was found, the surrounding matrix remained at almost the same thickness due to the reduced size of the NbC grains.

The changes in microstructure are found to be similar to those observed in the TiC system. One important difference is the thickness of the matrix, which is much thinner in the case of NbC/a-C compared to TiC/a-C. This can be explained by a larger homogeneity range for TiC, which makes it easier to create C vacancies and therefore allow more free C to cluster during growth. The thinner matrix can be used to explain the lower resistivity of NbC/a-C ($260\text{--}1200\ \mu\Omega\text{-cm}$) compared to TiC/a-C ($1200\text{--}1600\ \mu\Omega\text{-cm}$) since an amorphous C matrix softens the structure and is less conducting than the MeC grains. Also, the contact resistance of the best Nb-C film ($140\ \mu\Omega$) is good and comparable to a Ag reference ($45\ \mu\Omega$) at a contact force of 100 N.

I have thereby shown that nanocomposites consisting of NbC/a-C can function as an electrical contact material and that the electrical and mechanical properties can be tuned by a suitable choice of composition.

7.2 Ternary systems

The addition of a third element into a metal carbide increases the complexity, but also the ability to design a multifunctional material. For example, Si is sometimes added in the well-studied Ti-C system to further tailor the properties of the formed Ti-Si-C nanocomposite material by decreasing the grain size of the TiC grains [7]. In the formed nanocomposite system some Si can be incorporated into the TiC_x crystalline grains. There are, however, different opinions on whether Si is incorporated on the Ti [8,9] or C [10-13] site.

To solve this problem and to investigate how Si segregates to form a nanocomposite structure, I used a model system of epitaxial TiC_x ($x\sim 0.7$) into, which small amounts of Si is incorporated (**Paper 2**). Here, the Ti-Si-C films were deposited from elemental targets at a substrate temperature of $350\ ^\circ\text{C}$. The voltage on the Si target was changed between the depositions in order to control the amount of incorporated Si. For up to 4 at.% Si, the epitaxy is at least locally sustained. XRD shows an expansion of the lattice parameter of the TiC_x indicating that some of the Si is incorporated on the C sites in the TiC_x to form a $\text{Ti}(\text{Si},\text{C})$ phase. The formation of a $\text{Ti}(\text{Si},\text{C})$ phase is supported by theoretical calculations of the preferred position of Si if the Si atoms are trapped in a cubic $\text{TiC}_{0.75}$ structure. For an increasing Si content above and equal to 4 at.%, the epitaxy is gradually lost and the Si segregates to the column boundaries of the TiC_x grains forming a nanocomposite structure.

As seen in **Paper 2**, an increase of Si hinders the growth of TiC and this is also generally observed for other MeC in other Me-Si-C systems. A systematic study of the influence of Si on the structure and mechanical properties has been made in the Zr-Si-C system [14,15]. The results show that a transition to a completely

amorphous material occurs for Si contents higher than 15 at.%. For the amorphous structure, a random network of different bonds could be modelled. The results also show that some mechanical properties depend on the amount of strong Si-C bonds in the structure.

I wanted to see if these results are also true for other Me-Si-C systems and in **Paper 3** I therefore investigated Nb-Si-C thin films. In this paper two series of Nb-Si-C thin films were deposited from elemental targets with DC magnetron sputtering at a substrate temperature of 300 °C. In the first series the C content was kept constant at ~55 at.% and the Nb/Si ratio was varied. In the second series the Si content was instead fixed ~45 at.% and the C/Nb ratio was changed.

For Si contents below 25 at.%, the films have a nanocomposite structure with cubic NbC grains embedded in an amorphous matrix of SiC and C. With a Si content above 25 at.% the films are amorphous when viewed in HRTEM. With increase of Si the resistivity increases from 211 $\mu\Omega\cdot\text{cm}$ to 3215 $\mu\Omega\cdot\text{cm}$. A drop in the hardness was also observed with hardness between 18-19 GPa for the Si containing films compared to 22 GPa for the binary Nb-C film. The mixture of chemical bonds in the amorphous Nb-Si-C films suggests that the structure is similar to the network structure seen in the Zr-Si-C films. The amount of Si required to form an amorphous Me-Si-C film is, however, higher in the case of Nb-Si-C (>25 at.%) than for Zr-Si-C (>15 at.%). This indicates a lower glass-forming ability for Nb compared to Zr.

While the hardness of the Nb-Si-C and Zr-Si-C films seems to depend on the amount of Si-C bonds rather than the choice of transition metal, the elastic modulus shows a dependency on the used transition metal. My results thus suggest that it should be possible to produce high wear resistant films (high H/E and H^3/E^2) by appropriate choice of composition and transition metal.

To extend the knowledge of ternary Me-C based systems and study the influence of different components I decided to change Si for Ge as A-component in the Nb-A-C system (**Paper 6**). Nb-Ge-C thin films were therefore deposited from elemental targets by dc magnetron sputtering at a substrate temperature of 200 °C. The Ge content was changed between 0-30 at.% in three series with different C/Nb ratios. The films were found to have a nanocomposite structure with substoichiometric NbC_x in a nm-thick matrix of amorphous C and Ge. The binary Nb-C films have a (111) preferred crystallographic orientation with NbC_x grains that are elongated in the growth direction. With the addition of Ge the grains becomes equiaxed and with random orientation. A small addition of Ge gives a more porous structure, but with further increase in the Ge content the films show a less columnar and denser structure. Due to the porosity of the material a high level of O contamination (up to 22 at.%) was seen. The porosity and oxygen content affects the resistivity, which varies between 470-1735 $\mu\Omega\cdot\text{cm}$ depending on the porosity. The lowest contact resistance (1.7 m Ω) was found for the binary films. The contact resistance was not affected by the change in porosity, but increased with Ge content. Looking at the influence of Ge compared to Si, Ge in a similar way to Si decreases the size of the crystalline NbC grains. However, a transition to

a completely amorphous material is never seen even at high Ge contents (~30 at.%). Another dissimilarity is that while Si bond to C and form a matrix of a-SiC, Ge tends to bond to Ge.

7.3 Artifacts from characterization

I discovered a potentially important problem of introducing electron-beam-induced crystallization as an artifact when studied amorphous Nb-Si-C samples in high resolution TEM. The possibility of such artifacts is known to be induced if the interaction between the electron-beam and the sample is too strong [16-18], but not well reported for ternary transition metal carbides. Since TEM offers high spatial resolution it is used as a standard technique to characterize the structure of amorphous and nanocrystalline materials and it is therefore of general interest to know if ternary transition metal carbides are susceptible the energetic electron irradiation during HRTEM studies.

Thus, in **Paper 4** and **5** effects of the electron beam in high resolution transmission electron microscopy under normal imaging conditions on the amorphous phase in transition metal silicon carbide are studied. For this purpose, two different transition metals, Zr and Nb were selected. The electron beam induced formation of crystalline MeC grains in both the Nb-Si-C and the Zr-Si-C films. The causes of the crystallization were investigated by studying at the effect of different dose as well as different energy of the electrons in the electron beam. It was found that different beam currents with the same dose generate similar crystallization. If the electron energy is lowered from 200 keV to 80 keV, the crystallization is remarkably reduced for the same dose. The effect of heating was tested by *in-situ* annealing of the sample in the TEM. It was found that the crystallization process started between 400-600 °C. However, this process was much slower than for the beam-induced crystallization. The conclusion is that heating is not the main cause of the crystallization. Instead the energy dependence suggests that the crystallization is produced by a knock-on process, where energy from one elastically scattered beam electron is transferred to one of the specimen atoms causing displacement of this atom.

Looking at compositional effects it is clearly seen that the Zr-containing specimens are much more stable than the Nb-Si-C specimens. Also, a higher amount of Si stabilizes the amorphous structure, but to much less extent.

Kádas et al. [15] showed with good agreement to experimental data that the structure of the amorphous state of Zr-Si-C can be simulated as a random distribution of atoms. Since the relative amounts of bonds in XPS are similar in the Nb-Si-C case I assume that the random distribution also applies for Nb-Si-C (**Paper 3**). During electron irradiation mainly C and possibly also Si are displaced by collisions with electrons from the electron beam. This creates density fluctuations that increase the ability of the surrounding Me atoms to move into this place and form a carbide crystallite by nucleation and growth. The growing MeC grains requires less molar volume compared to the starting amorphous matrix,

which increase the length by which atoms from the neighboring matrix need to migrate. This, together with the increase in concentration of Si at the carbide/matrix interface reduces the crystallization rate. At a certain build-up in Si concentration, further grain growth is no longer possible and the crystallization eventually stops. Since the amorphous Nb-Si-C films are less stable than the amorphous Zr-Si-C films nucleation of NbC grains will occur more often resulting in a larger number and smaller sized grains.

The time to obtain a critical dose in the Nb-Si-C case was only a few minutes. Therefore, I draw the conclusion that great care should be used in imaging these kinds of materials for a correct structure characterization. Also, the effect of ion irradiation caused by the ion milling in the sample preparation were investigated in **Paper 4** since ion milling have been shown to introduce artifacts in XPS C1s spectra of metal carbides [19]. This was done by comparing samples made in the conventional way with samples made by the small angle cleavage technique. However, no large difference between the two methods was found.

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