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Nanoscale structure forming processes

Metal thin films grown far-from-equilibrium

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The cover image shows a high angle annular dark field scanning transmission electron microscopy micrograph of elongated Ag-Cu atomic islands supported on a SiO₂ substrate. Intensity variation within each island stems from mass contrast caused by segregation into Ag- and Cu-rich domains. Image courtesy of Dr. Robert D. Boyd.

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

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Till mormor.

Thin film growth from the vapor phase has for a long time intrigued researchers endeavouring to unravel and understand atomistic surface processes that govern film formation. Their motivation has not been purely scientific, but also driven by numerous applications where this understanding is paramount to knowledge-based design of novel film materials with tailored properties.

Within the above framework, this thesis investigates growth of metal films on weakly bonding substrates, a combination of great relevance for applications concerning e.g., catalysis, graphene metallization and architectural glazing. When metal vapor condenses on weakly bonding substrates three dimensional islands nucleate, grow and coalesce prior to forming a continuous film. The combined effect of these initial growth stages on film formation and morphology evolution is studied using pulsed vapor fluxes for the model system Ag/SiO₂. It is shown that the competition between island growth and coalescence completion determines structure evolution. The effect of the initial growth stages on film formation is also examined for the tilted columnar microstructure obtained when vapor arrives at an angle that deviates from the substrate surface normal. This is done using two metals with distinctly different nucleation behaviour, and the findings suggest that the column tilt angle is set by nucleation conditions in conjunction with shadowing of the vapor flux by adjacent islands. Vapor arriving at an angle can in addition result in films that exhibit preferred crystallographic orientations, both out-of-plane and in-plane. Their emergence is commonly described by an evolutionary growth model, which for some materials predict a double in-plane alignment that has not been observed experimentally. Here, an experiment is designed to replicate the model's growth conditions, confirming the existence of double in-plane alignment.

New and added film functionalities can further be unlocked by alloying. Properties are then largely set by chemistry and atomic arrangement, where the latter can be affected by thermodynamics, kinetics and vapor flux modulation. Their combined effect on atomic arrangement is here unravelled by presenting a research methodology that encompasses high resolution vapor flux modulation, nanoscale structure

probes and growth simulations. The methodology is deployed to study the immiscible Ag-Cu and miscible Ag-Au model systems, for which it is shown that capping of Cu by Ag atoms via near surface diffusion processes and rough morphology of the Ag-Au growth front are the decisive structure forming processes in each respective system.

The results generated in this thesis are of relevance for tuning structure of metal films grown on weakly bonding substrates. They also indicate that improved growth models are required to accurately describe structure evolution and emergence of a preferred in-plane orientation in films where vapor arrives at an angle that deviates from the substrate surface normal. In addition, this thesis presents a methodology that can be used to identify and understand structure forming processes in multicomponent films, which may enable tailoring of atomic arrangement and related properties in technologically relevant material systems.

Populärvetenskaplig sammanfattning

Genom att belägga ett föremål med ett tunt lager material, en så kallad *tunnfilm*, kan man förändra eller förbättra föremålets egenskaper. Tunnfilmer är vanligtvis bara några få mikrometer (tusendels millimeter) tjocka och ibland betydligt tunnare än så, vilket gör att vi inte kan se dem med blotta ögat. Denna tjocklek kan jämföras med den av ett människohår som är kring hundra mikrometer (tiondels millimeter). Trots att tunnfilmerna är så pass tunna kan de exempelvis förhindra uppkomsten av repor och reflexer på glasögon, minska friktionen mellan motordelar, eller minska energianvändningen i byggnader genom användandet av lågemissiva fönster. Tunnfilmer är också en förutsättning för mikroelektroniken som ligger till grund för dagens datorer, smartphones och bärbara elektronik som många av oss tar för givna och ibland inte skulle kunna tänka oss ett liv utan. De många användningsområdena för tunnfilmer tillsammans med deras betydelse i dagens samhälle gör att tunnfilmsindustrin omsätter miljardbelopp varje år.

Ett vanligt sätt att skapa tunnfilmer är genom att omvandla ett material i fast form till gasform och sedan låta gasen kondensera på föremålet som ska beläggas, atom för atom. Ungefär på samma sätt kondenserar vattenånga under morgontimmarna på exempelvis ett biltak för att bilda dagg. När atomerna har kondenserat på föremålet byggs tunnfilmen upp i flera steg. Först rör sig de kondenserade atomerna över ytan tills de stöter på varandra vilket leder till att kärnor bildas på ytan. Kärnorna växer sedan i storlek och skapar ett ölandskap på atomnivå. Vid någon tidpunkt har öarna vuxit så pass mycket att de börjar stöta på varandra. Då startas en process där atomerna i öarna förflyttar sig för att försöka bilda en enda ö. Tiden det tar att slutföra den här processen ökar med öarnas storlek och vid någon storlek kommer den inte hinna färdigställas. Vid det här laget består tunnfilmen av sammanbundna önätverk som är separerade av tomrum. Genom att belägga fler atomer fylls tomrummen igen och sluter tunnfilmen så att den blir kontinuerlig och heltäckande. Alla dessa processer påverkar filmens slutliga struktur och är därför viktiga att förstå för att kunna skräddarsy filmernas egenskaper. För att illustrera vikten av denna förståelse kan vi till exempel betrakta de lågemissiva fönster som nämndes ovan. På fönstrens glasrutor

appliceras vanligen en tunn silverfilm för att reflektera solens infraröda strålar som annars tränger in och värmer upp insidan av byggnader under varma sommar dagar, samtidigt som värme från insidan hindras från att sippra ut under kalla vinter dagar. Om silverfilmen är för tunn fyller den inte någon funktion, och om den är för tjock kommer den istället att fungera som en spegel vilket skulle göra det omöjligt att se ut genom fönstret. Istället efterfrågas i just detta fall en film som är tillräckligt tunn för att släppa igenom synligt ljus samtidigt som den är tillräckligt tjock för att ha en hög elektrisk ledningsförmåga som gör att de infraröda strålarna blockeras. För att uppnå detta behöver vi införskaffa en god förståelse för filmernas tillväxt och de processer som är avgörande för filmens struktur.

Det vanligaste sättet att belägga tunnfilmer i allmänhet är genom att hela tiden tillföra nya atomer till den växande filmen. De dynamiska processerna som leder fram till en kontinuerlig film kan å andra sidan påverkas om belägningsflödet stängs av under vissa tider så att nya atomer bara tillförs under korta tidsperioder. Tidigare studier har fokuserat på vart och ett av stegen som leder fram till en kontinuerlig film, men det är ju deras kombinerade effekt som avgör filmens slutliga struktur. Denna kombinerade effekt har jag undersökt i mitt arbete där jag har belagt silver på kiseldioxid. För detta vanligen använda modellsystem visar jag att filmens tillväxt bestäms av tiden då flödet av nya atomer är avstängt i relation till hur snabbt öarna på ytan kan slå sig samman. En kortare tid innebär att få eller inga öar hinner slå sig samman medan en längre tid ger möjlighet till fler sammanslagningar. Detta innebär att filmens struktur kan kontrolleras genom att exempelvis styra hur tjock film som krävs för att den ska bli kontinuerlig. Ju fler ösammanslagningar, desto tjockare film.

Ytterligare ett sätt att förändra strukturen hos filmerna är genom att låta flödet av atomer falla in från sidan av belägningsobjektet istället för rakt framifrån som annars är vanligast. Det gör att baksidan av de växande öarna skuggas från belägningsflödet vilket hindrar atomer från att kondensera där. Öarna kommer därför bara kunna fortsätta växa på platser som inte är skuggade. Det leder till en struktur som består av separerade kolumner som lutar mot belägningsflödet. Vinkeln som kolumnerna lutar med används ofta som ett sätt att försöka förstå hur kolumnerna växer och vilka processer som är inblandade. Vanligen observeras det att olika material lutar olika mycket trots att de växt under samma förutsättningar. För att förklara det har jag föreslagit att lutningen bestäms redan under kärnbildningen vilket tidigare har förbisetts helt och hållet. Denna kunskap skulle kunna användas till att skapa bättre designade tunnfilmer, men också ge en ökad förståelse som kan vara av stor vikt om tillväxten istället simuleras av datorer.

Förutom att uppnå en speciell struktur på filmerna när belägningsflödet faller in från sidan ordnar sig i vissa fall atomerna på samma sätt i förhållande till varandra i alla kolumnerna. För att förstå vikten av denna ordning kan vi för en stund tänka oss att vi ska lägga ett pussel. När vi kastar ut alla pusselbitarna på bordet kommer de att ligga i ett enda virrvarr. I ett första steg börjar vi med att vända alla bitarna åt rätt håll så att vi ser vad de föreställer. Vi har nu skapat viss ordning, men bitarna ligger fortfarande huller om buller i förhållande till varandra. För att skapa fullkom-

lig ordning behöver vi alltså sätta ihop alla pusselbitarna på rätt sätt. Tillsammans bildar de då ett större ihållande mönster. På samma sätt kan kolumnerna växa så att de passar ihop med varandra som ett stort pussel när beläggning sker från sidan. En film med kolumner som är ordnade på detta sätt har därför ungefär samma egenskaper som en film som bara skulle bestå av en enda kolumn som sträcker ut sig utan avbrott längs med föremålet som belagts. Att skapa ytor som motsvarar en enda kolumn är dessvärre både dyrt och svårt, i synnerhet när ytans storlek ökar, men vissa typer av tunnfilmer, såsom halvledare och supraleidare, kräver dem för att fungera önskvärt. För att spara pengar och möjliggöra större ytor kan man därför belägga ett billigare föremål med ordnade kolumner innan dessa speciella typer av tunnfilmer appliceras. I min forskning har jag testat den vedertagna modell som beskriver hur ordningen uppkommer. De resultat som jag fått fram indikerar att det finns ytterligare processer inblandade i utvecklingen av kolumnernas ordning än de som för närvarande är inkluderade i modellen. Om vi skulle kunna få förståelse för dessa processer skulle vi förhoppningsvis kunna förbättra tunnfilmernas egenskaper och därmed också egenskaperna av tunnfilmerna som appliceras ovanpå.

Ibland räcker det inte med ett enda atomslag för att uppnå de efterfrågade egenskaperna hos en tunnfilm och vi kan då behöva kombinera flera olika ämnen med varandra. I de fallen avgörs tunnfilmernas egenskaper till stor del av de ingående ämnena, men också av hur de är placerade i förhållande till varandra. Exempelvis kan vi blanda dem med varandra, eller så kan vi placera dem i alternerande lager likt lagren i en tårta. För att designa strukturen och skräddarsy egenskaperna hos en tunnfilm som består av flera olika ämnen behöver vi alltså förstå vilka processer som är aktiva och ansvariga för de olika atomernas placering. I mitt arbete har jag presenterat en metod som gör det möjligt att erhålla denna kunskap. För att visa att metoden fungerar använde jag mig av två olika modellsystem som båda bestod av två olika metaller. Vanligtvis används inte dessa modellsystem i någon tillämpning, men genom att ha visat att metoden fungerar är förhoppningen att den senare ska appliceras på andra tillämpade system, exempelvis optiska och magnetiska, för att förbättra deras egenskaper.

Sammanfattningsvis kan vi konstatera att tunnfilmer har ett brett användningsområde och är vanligt förekommande i vår omvärld. Resultaten från min forskning har bidragit till en ökad förståelse för de processer som bestämmer tillväxten av tunnfilmer, deras struktur och atomernas placering i förhållande till varandra. Förhoppningen är att denna kunskap ska leda till större möjligheter att designa tunnfilmer och på så sätt skräddarsy deras egenskaper efter den tilltänkta applikationen.

Preface

This dissertation is the result of my doctoral studies carried out between 2011 and 2014 in the Plasma and Coatings Physics Division, and between 2014 and 2016 in the Nanoscale Engineering Division at the Department of Physics, Chemistry and Biology, Linköping University, Sweden. The contents of the introductory chapters, which are intended to provide the reader with an overview of the research field and the methods employed, are to a large extent based on, and expanded from, my previously published Licentiate Thesis titled *Thin film growth using pulsed and highly ionized vapor fluxes* (Licentiate Thesis No. 1641, Linköping Studies in Science and Technology). The initial chapters are succeeded by the results from the research performed, which are presented in appended papers.

My research has been financially supported by Linköping University via the LiU Research Fellows Program, 2011-2015 and the LiU Career Contract (Dnr-LiU-2015-01510), 2015-2020. In addition, travel grants from Ångpanneföreningens Forskningsstiftelse (ÅForsk, ref. nos. 12-095 and 14-593) and the Royal Swedish Academy of Sciences (appl. no. PH2016-0007) have supported attendance at international conferences.

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Outside of academia, I would like to thank family and friends for support, encouragement and for bringing joy to my life. One day I hope to have gathered enough knowledge to actually explain what I do in a sensible manner. One day. I would also like to thank my four-legged friends for all hours spent together in the forest, for teaching me all there is to know about mindfulness, and for implying that rain is simply water in motion.

To my lovely daughter Linnea, you are a source of immeasurable joy. Last, but certainly not least, to my wonderful wife Jessica. I am thankful beyond what words can express. I love you!

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CHAPTER 1

Introduction

Throughout the history, materials have proved to be a vital component in shaping the development of mankind. This is manifested by historians naming time periods by the most prominent material used or discovered during that time, like e.g., the Stone Age, the Bronze Age and the Iron Age [1, p. 3]. The emergence of the materials employed during these different time periods enabled new and improved material properties, yielding e.g., better tools and weapons. The search for new and improved materials in order to advance society has continued ever since and today there is an ever increasing demand in areas like energy, environment, health and modern information technology, just to mention a few examples. This is all comprised in the interdisciplinary field of materials science, which aims at understanding the relationships between structure, property, performance and synthesis methods to improve existing materials as well as to discover new ones.

1.1 Thin films

A material generally consists of a bulk and at least one surface. Its bulk properties might be superior, but since the surface interacts with the surroundings the overall properties can still be inferior. One way to overcome this issue is by applying another material with superior surface properties to its surface and in that way combine superior surface and bulk properties. The added material does not need to be thick to drastically improve the surface properties of the bulk material, a thin film ranging from a single atomic layer up to several micrometers (~ 10000 atomic layers) in thickness is sufficient. This can be compared to the thickness of a human hair which is around one hundred micrometers [2, p. 5]. In addition to achieve improved surface properties of the bulk, thin films can also be applied to add new functionalities to a material and in that way instead alter its properties.

The existence of man-made thin films is known already from the fifth millennium B.C. when the Egyptians decorated statues and artifacts with thin Au layers [3]. The applicability of using thin films has since then evolved far beyond that of decorative purposes and today they are a vital part of our modern society where they are used e.g., to reduce heat transfer in low emissivity windows, for protective and wear-resistant purposes on tools, as anti-reflective and scratch resistant layers on eyeglasses and lenses, and for low friction and wear resistant purposes on hip implants and engine parts.

1.1.1 Film formation

A common way to form thin films is to vaporize a solid source material that condenses in an atom-by-atom fashion onto a bulk material, referred to as substrate. The adsorbed atoms, i.e., the adatoms, diffuse on the substrate surface until they meet others. As this happens, they nucleate and form atomic islands that grow in size, impinge on each other and coalesce before forming a continuous film. These initial growth stages, i.e., nucleation, growth and coalescence, thus set characteristic length scales of the films, such as e.g., distribution of island sizes and separation, that in turn determine properties like e.g., electrical conductivity [4], surface roughness and continuous film formation thickness [5, p. 495]. The above described growth process is commonly considered in terms of thermodynamics, which steer the system towards thermodynamic equilibrium. For far-from-equilibrium conditions where a majority of films today are grown, kinetic barriers may however hinder the emergence of the thermodynamically most stable configuration. This can drastically alter the characteristics of the initial growth stages and hence the microstructure of the films. Understanding the interplay between kinetics and thermodynamics is thus paramount to enable knowledge-based structure-property tuning of films grown far-from-equilibrium.

The initial growth stages are particularly pronounced for metals grown on weakly bonding substrates since the metal in that case starts to grow as well-separated three dimensional islands on the substrate surface [6, p. 555]. This causes the different stages to appear more separate during film formation and they do hence show distinct characteristics in time as growth proceeds. Understanding these basic surface processes is intriguing from a pure scientific point of view, but there is also a driving force from technological applications in e.g., microelectronics [7], architectural glazing [8], plasmonics [9], catalysis [10] and metallization of graphene [11]. In addition, pure metals typically offer a less complex chemistry during growth as well as in the vapor phase as compared to e.g., oxides or nitrides where an additional reactive gas needs to be added to the process. Metals are thus both technologically relevant and highly suitable as model systems in order to understand thin film growth processes.

The most common way to grow thin films from the vapor phase is by supplying a continuous flux of atoms to the substrate surface. Additional control can however be obtained by changing the temporal profile of the flux and instead only supply atoms during well-defined periods of times. The use of such pulsed fluxes affects

growth dynamics and previous studies have unravelled the underlying physics that determine the effect of pulsed vapor fluxes on the initial film formation stages and how they individually can be manipulated [12–15]. Understanding their combined effect on film formation is however required for tailoring film structures and related properties.

Another way to affect structure formation of thin films is by letting vapor atoms arrive at an angle that deviates from the substrate surface normal. The areas behind the initially formed islands do then get shadowed from the vapor flux due to the line-of-sight characteristics of the deposition process, which means that no atoms from the vapor condense in these areas [16, 17]. This leads to growth of separate columns that tilt towards the vapor source. Films grown in this way do thus exhibit characteristic geometrical structures that intrinsically yield anisotropic properties, and on top of that they can also possess large surface areas. This makes them applicable in areas of e.g., photovoltaic cells, sensors and optics [16, 17]. To enable design of these structures and the related properties one needs to understand the structure forming processes that are decisive for film formation. Much efforts have so far been directed towards the effect of growth conditions [18–20], but even as growth is performed at similar conditions different materials are commonly observed to grow with different column tilt angles [21–23]. One possibility could be that this disparity is caused by growth differences during the initial formation stages, but any such effects have not yet been addressed.

Letting vapor arrive at a non-zero angle with respect to the substrate surface normal can also, in some cases, lead to a biaxial alignment where the columnar structure exhibits preferred crystallographic orientations, both out-of-plane and in-plane [24]. In practice this means that the film structure is similar to that of a single crystal, making biaxially aligned films suitable as cost-effective large area buffer layers for superconducting [25, 26] and semiconducting [27–29] films. To explain the development of the in-plane alignment an evolutionary growth model has been proposed [24]. For some materials it predicts a double in-plane alignment that has not been observed experimentally. This could be due to the fact that some of the initial growth characteristics are overlooked in the proposed model.

1.1.2 Atomic arrangement

Sometimes the properties offered by the single elements do not meet the requirements and one might need to alloy multiple elements with each other. In that case, film properties are to a large extent determined by the different elements and their composition, but also by the atomic arrangement of the constituents. One way to tune the atomic arrangement is by employing temporally modulated fluxes. To achieve this modulation, shutters are typically placed in front of the vapor sources that sequentially open and close in order to grow layered structures where different materials are stacked on top of each other. This allows for improved e.g., optical [30], magnetic [31] and mechanical [32] properties. The use of temporally modulated fluxes with higher resolution than that offered when using shutters has indicated that

it is possible to control the atomic arrangement at shorter length scales than that typically found in multilayered structures [33]. This would allow for further tailoring of microstructure and related film properties if the structure forming processes governing growth of multicomponent films via modulated fluxes would be understood.

1.2 Research goal, strategy and impact

The overall goal with this research is to contribute to an increased fundamental understanding of structure forming processes in metal thin films grown from the vapor phase at far-from-equilibrium conditions. This is realized by establishing the individual and combined effect of the initial growth stages on film formation and morphology evolution of metal films grown on weakly bonding substrates in Papers 1 and 2, using pulsed vapor fluxes for the model system Ag/SiO₂. The effect of the initial growth stages on structure evolution of films grown from vapor fluxes arriving at a non-zero angle with respect to the substrate surface normal is then acquired in Paper 3, using two metals with distinctly different nucleation behaviour. The implication of overlooking part of the initial growth characteristics in the evolutionary growth model describing development of a preferred in-plane alignment is further assessed in Paper 4, by experimentally replicating the model's growth conditions. Finally, the combined effect of thermodynamics, kinetics and high resolution vapor flux modulation on atomic arrangement is obtained in Papers 5 and 6. This is accomplished by presenting a research methodology that encompasses high precision flux modulation, nanoscale structure probes and growth simulations, and employing it to study miscible and immiscible metal binary model systems.

The knowledge and understanding generated in this thesis is of relevance for structure tuning of metal films grown on weakly bonding substrates and can be used as basis for future studies of thin film growth dynamics. The presented results do also suggest that the current models describing growth evolution and development of a preferred in-plane alignment in films grown from vapor fluxes arriving at an angle need to be improved in order to provide an accurate description of their formation. In addition, the presented methodology for identifying and understanding structure forming processes in multicomponent materials may enable tailoring of atomic arrangements and related properties.

1.3 Outline of this thesis

This first chapter is an introduction to the work carried out in this thesis. It is followed by a description of thin film formation and the processes involved in chapter two. The third chapter gives an introduction to the different experimental synthesis methods employed, whereas chapter four briefly covers the simulation counterparts. In chapter five, the characterization techniques utilized are reviewed, before my contributions to the field are summarized in chapter six.

CHAPTER 2

Thin film growth

Thin film growth on a substrate surface commonly proceeds by nucleation of atomic islands that grow in size, impinge on each other and coalesce before forming a continuous film. In order to understand the atomistic processes involved during film formation it is informative to first consider epitaxial film growth. Epitaxy refers to growth of a crystalline film on top of a crystalline substrate that imposes a specific crystalline orientation to the film. It can further be divided into homoepitaxy, film and substrate materials are the same, and heteroepitaxy, where different materials are used as film and substrate. For many applications the substrates are however not crystalline. In those cases, the film is instead typically found to be polycrystalline, i.e., to consist of many crystallites of different sizes and orientations. Even then, understanding epitaxy is still relevant since growth on each individual crystallite is homoepitaxial.

One of the most well-known models of thin film growth was first classified by Bauer in 1958 [34], and concerned the epitaxial growth of films at conditions near thermodynamic equilibrium. The near-equilibrium growth infers that the deposited atoms possess sufficient energy to reach their lowest energy positions, and the film is thus able to grow according to its equilibrium shape. This is in contrast to far-from-equilibrium conditions where kinetic barriers can impede the thermodynamically favored configurations. Understanding thin film growth at conditions far-from-equilibrium thus starts with a treatment of the opposite situation owing to the natural driving force towards equilibrium. Hence, this chapter starts with a brief introduction to near-equilibrium growth before entering the fascinating world of far-from-equilibrium processes.

2.1 Near-equilibrium growth

At conditions near thermodynamic equilibrium the microstructural evolution during epitaxial growth is dictated by the balance between the surface energies of substrate (γ_s), film (γ_f) and film-substrate interface (γ_i) [34]. Typical for epitaxial growth is that $\gamma_s \geq \gamma_f + \gamma_i$, which means that the film completely wets the substrate in order to minimize the surface energies and hence grows in a layer-by-layer fashion (also known as the Frank van der Merwe growth mode, Fig. 2.1 (a)). For the case of homoepitaxy equality holds in the above relation since $\gamma_i = 0$ [35, p. 18]. On the contrary, if $\gamma_s < \gamma_f + \gamma_i$ the surface energy is instead minimized by bunching up and growing mounds or islands of the deposit (referred to as Volmer-Weber growth mode, Fig. 2.1 (b)). A third growth mode also exists where the film starts to grow in a layer-by-layer fashion, but after a critical thickness strain relaxation causes the formation of three dimensional islands on top of the initial layers. The strain relaxation can occur either coherently or incoherently, where the latter occurs by formation of misfit dislocations under the islands that relieve the strain energy [36]. This growth mode is known as layer-plus-island growth or Stranski-Krastanov (Fig. 2.1 (c)).

Fig. 2.1. Schematic illustration of different growth modes depending on relation between surface energies. (a) Layer-by-layer (Frank van der Merwe), (b) island formation (Volmer-Weber) and (c) layer-plus-island (Stranski-Krastanov).

It should be pointed out here that these three growth modes initially were developed for epitaxial systems grown near-equilibrium, but nowadays they are commonly used in the literature to also describe the morphology of films grown far-from-equilibrium. One should however keep in mind that the physical reason for the observed growth behaviour might be different, which will become apparent later on.

2.2 Far-from-equilibrium growth

Today, the majority of thin films are grown from the vapor phase at conditions far-from-equilibrium. This means that in addition to the surface energy balance discussed in the previous section (Sec. 2.1) kinetic limitations can also be decisive in determining the growth evolution of the films. The basic concept of a kinetic limitation is that an activation energy barrier separates two states. Depending on the amount of energy that is needed for the transition, the rate of the reaction changes,

where a higher energy barrier corresponds to a lower rate. This means that thermodynamically unstable states can be metastable at far-from-equilibrium conditions. These types of kinetic processes, together with their implications on film growth, are discussed in the following sections.

2.2.1 Surface diffusion

Film growth is initiated by condensation of atoms from the vapor phase onto a substrate surface. This causes atoms to transfer most of their energy into lattice vibrations before being adsorbed and referred to as adatoms. On the surface, they experience a potential energy landscape originating from the substrate atoms. Due to fluctuations in this energy landscape some sites offer more energetically stable positions than others and act as preferential adsorption sites. Adatoms are able to move between these sites if they possess sufficient energy to overcome the activation energy barrier for surface diffusion, E_D , that separates neighbouring sites. This process is known as surface diffusion and can be described as a two-dimensional random walk between adjacent adsorption sites. The rate at which these events occur is described by the adatom jump rate, ν , as [37, p. 17]

$$\nu = \nu_0 \exp\left(-\frac{E_D}{k_B T}\right) \quad (2.2.1)$$

at a temperature T . ν_0 is a constant known as the attempt frequency (typical value of $\sim 10^{12} \text{s}^{-1}$ [38, p. 87]) and k_B is the Boltzmann constant. For the typical distance covered in a single jump, a ,[†] the surface diffusion coefficient D is given by the relation [37, p. 17]

$$D = \frac{1}{4} a^2 \nu = \frac{1}{4} a^2 \nu_0 \exp\left(-\frac{E_D}{k_B T}\right), \quad (2.2.2)$$

where the factor $1/4$ accounts for the two-dimensional nature of the diffusion process. As is evident from Eq. (2.2.2) adatom diffusion can be increased by simply raising T . The other main deciding factor is E_D that is determined by the interaction between adatoms and the underlying surface atoms.

2.2.2 Nucleation

Adatoms on an atomically flat surface can either desorb back to the vapor or diffuse until they encounter other adatoms that bond to each other and form a cluster. The cluster can, in turn, dissolve back into the two-dimensional adatom gas or form a stable nucleus. The latter occurs if the cluster size is larger than a critical value i^* , typically expressed in number of atoms. For low growth temperatures i^* is often found to be equal to one [6, pp. 567-579], meaning that a nucleus consisting of two or more atoms are more likely to grow than to dissociate.

[†]Typically, a refers to nearest-neighbour hopping distance, which for the case of metals is $\sim 3 \text{ \AA}$ ($1 \text{ \AA} = 10^{-10} \text{ m}$).

The nucleation process described above is typically characterized by the island density, N , i.e., the number of atomic islands per surface unit area. In the early stages of growth, N depends predominantly on the amount of deposited material [37, p. 28]. This is known as the transient nucleation regime and is valid until an appreciable amount of diffusing adatoms are captured by already existing islands. As this happens the steady-state nucleation regime is entered and N scales as [37, p. 29]

$$N \propto \left(\frac{F_{avg}}{D} \right)^\chi \quad (2.2.3)$$

for a continuous supply of atoms from the vapor phase. In Eq. (2.2.3) F_{avg} is the time averaged deposition rate and χ is a scaling exponent that depends on i^* and the dimensionality of the growth process. For three-dimensional islands[‡] grown on a two-dimensional surface χ is given by the relation [37, p. 49]

$$\chi = \frac{i^*}{i^* + 2.5} \quad (2.2.4)$$

which yields $\chi = 2/7 \approx 0.286$ for $i^* = 1$. From Eq. (2.2.3) it is evident that N can be increased by either increasing F_{avg} or decreasing D , where the latter can be accomplished by simply lowering the growth temperature (cf. Eq. (2.2.2)). It should, however, be noted that D depends exponentially on T , which means that F_{avg} needs to be varied many orders of magnitude to yield the same result as obtained when varying T .

The nucleation characteristics can also be altered by chopping a continuous vapor flux into well-defined pulses characterized by their active time, t_{on} , instantaneous rate, F_i , and frequency, f . This yields an additional kinetic handle for nucleation depending on the interplay between the time scale of the vapor flux and the time scale of the diffusing adatoms, as characterized by their lifetime, τ_m . The latter can be approximated as

$$\tau_m \approx \frac{\ell^2}{D} \quad (2.2.5)$$

if adatoms mainly disappear by diffusion into existing islands separated by a mean distance of 2ℓ [12]. In the case that $\tau_m \gg 1/f$, adatoms are still present on the surface between successive pulses (see Fig. 2.2 (a)) and the substrate experiences a continuous deposition flux $F_{avg} = F_i t_{on} f$, which means that N scales according to Eq. (2.2.3). In the other limiting case, adatom diffusion and nucleation happen almost instantly within a single pulse ($\tau_m \ll t_{on}$, Fig. 2.2 (c)), which implies that the substrate sees the instantaneous flux as if it would be continuous. This means that N scales as [12]

$$N \propto \left(\frac{F_i}{D} \right)^\chi \quad (2.2.6)$$

[‡]This is the typical growth mode for metals grown on insulating substrates, which is discussed more in Sec. 2.2.3.

Fig. 2.2. Schematic illustration of the three different nucleation regimes in pulsed deposition. In (a) $\tau_m \gg 1/f$, (b) $t_{on} < \tau_m < 1/f$ and (c) $\tau_m \ll t_{on}$. The solid line represents deposition and the dashed line the corresponding adatom density.

From this relationship it can be understood that for fluxes characterized by $F_i \gg F_{avg}$ (typical for pulsed deposition) N can be increased considerably, which for the growth of three-dimensional islands can lead to a lower surface roughness and an apparent two-dimensional growth. The two regimes are separated by a region where adatoms still diffuse between adjacent pulses, but disappear before the next pulse arrives ($t_{on} < \tau_m < 1/f$, Fig. 2.2 (b)). In this region N is independent of D and scales only with the deposition rate per pulse according to [12]

$$N \propto (F_i t_{on})^{1/2}. \quad (2.2.7)$$

The above nucleation regimes for pulsed deposition are derived for $i^* = 1$, but the correctness of using a constant time-independent value of i^* for time-dependent fluxes has however been questioned [39]. This is due to that the adatom density is not constant in between pulses. During the active part of the pulse there is an excess of adatoms that can prevent dissociation of the smaller islands, but as the pulse is

turned off and all adatoms are captured by preexisting islands, the smaller islands may need to dissociate in order to stabilize the larger ones. The rate at which the smaller islands are able to stabilize the larger ones would thus ultimately determine the evolution of i^* with time. Hence, this effect would be more pronounced for higher T and lower f .

2.2.3 Interlayer transport

As can be understood from the two previous sections (Secs. 2.2.1 and 2.2.2) E_D is a key component for determining both adatom diffusion and nucleation characteristics. Additional contributions to E_D can also arise from morphological features of the surface as depicted in Fig. 2.3 (a), where a step between two terraces is present. On top of terraces, adatoms experience E_D for diffusion between adjacent sites, but in order to descend a step a larger energy is required since an adatom in that case also needs to break a bond. This results in an additional barrier commonly referred to as the Ehrlich-Schwobell barrier, which together with E_D yields a total step-edge barrier, E_{SE} (see Fig. 2.3 (b)). On the contrary, ascending step edge sites instead act as trapping sites since they offer a higher coordination number and thus a more stable position. In addition to simple hopping across the edge, an adatom on top of a terrace can also descend and get incorporated into the layer below in an exchange process where an underlying atom is pushed out before the adatom takes its place [40, 41].

Fig. 2.3. (a) An adatom on top of a terrace with possible diffusion directions indicated by arrows. (b) Energy landscape of the surface in (a) as experienced by an adatom. The step-edge barrier E_{SE} and the diffusion barrier E_D are indicated in the figure.

The importance of the energy barriers E_D and E_{SE} can easily be understood by considering homoepitaxial film growth that, from the viewpoint of thermodynamics, exhibits potential to grow as layer-by-layer. In the case that adatom diffusion is high enough to overcome both E_D and E_{SE} , and that the diffusion length is much longer than the terrace width, adatoms are able to descend steps and are thus incorporated at step edges. This leads to a step flow growth where no nucleation events take place (Fig. 2.4 (a)). For diffusivities high enough to still overcome both E_D and E_{SE} , but with a considerably shorter diffusion length, two-dimensional islands nucleate on terraces. Since adatoms deposited on top of islands descend their edges, a complete layer is formed before any second layer nucleation events take place, resulting in layer-by-layer growth (Fig. 2.4 (b)). On the other hand, if E_{SE} hinders interlayer transport of adatoms three-dimensional mounds are formed on terraces (Fig. 2.4 (c)). Moreover, in the case of no intralayer diffusion (adatoms do not overcome E_D), diffusion is in practice turned off, and adatoms come to rest where they condense. This is known as self-affine growth and leads to an open structure with a large surface roughness (Fig. 2.4 (d)).

Fig. 2.4. Illustration of different growth modes depending on adatoms ability to overcome E_D and E_{SE} . (a) Step flow growth, (b) layer-by-layer growth, (c) mound formation and (d) self-affine growth.

Parts of this thesis concern the growth of metals on insulating substrates (e.g., SiO_2). For those systems, the metal typically grows as three-dimensional islands (Volmer-Weber type growth) due to low substrate surface energies as compared to that of the deposit, as well as that the deposit bonds more strongly to itself than to the substrate [6, p. 555 and 569]. The weak interaction with the substrate makes it more energetically favourable for an initially two-dimensional island, at a critical island size, to detach atoms from its edge, let them ascend the island and nucleate a second layer, as compared to continue growing a single layer [42]. The same type of critical island size has also been shown to exist for higher order layers [42], further supporting the three-dimensional growth. In addition, kinetic effects can promote three-dimensional growth as discussed above. For example, for the case of Ag diffusion on Ag(111), which is the low energy plane for Ag [43], $E_D \approx 0.10$ eV [44] and the

Ehrlich-Schwoebel barrier is ~ 0.13 eV [45]. This means that a bit more than twice the energy is needed for an adatom to descend a step as compared to for diffusion between adsorption sites. Adatoms can thus be trapped on top of islands and hence cause islands to grow three-dimensionally. These three-dimensional structures are highly relevant during growth of thin films and supported nanoparticles, and find technological applications in, e.g., plasmonic [9] and catalytic [46] systems, and magnetic devices [47].

2.2.4 Coalescence processes

2.2.4.1 Ostwald ripening

The nucleation process leaves atomic islands with different sizes on the substrate surface, where larger islands are more energetically stable since a lower fraction of the bonded atoms are present at the surface [48, 5, p. 395]. This means that atoms are more likely to detach from smaller islands, leading to a higher adatom density around the smaller islands as compared to the larger ones [49]. The difference in adatom densities yields a driving force for adatom diffusion from areas with high to areas with low density, as illustrated in Fig. 2.5. Large islands thus grow at the expense of smaller ones, which further accelerates the depletion of the smaller islands as the size difference increases. This process is called Ostwald ripening and results in a decreased island density and an increased average island size. It should however be noted that no additional sources of adatoms that eliminate the adatom density gradients can be present if the ripening process is to be active. In practice, this means that deposition of new adatoms from the vapor phase hinder the Ostwald ripening

Fig. 2.5. Illustration of Ostwald ripening, where adatom density gradients yield a preferred adatom diffusion direction towards larger islands.

process from being active [50]. For applications where no additional adatoms are supplied, such as e.g., in catalysis where small dispersed islands yield catalytic activity, Ostwald ripening can however be detrimental by decreasing the total island surface area such that the overall catalytic activity diminishes or even disappears with time [51].

2.2.4.2 Sintering

Adding more material to the substrate leads to growth of the atomic islands, stimulated by direct capture of atoms from the vapor phase as well as incorporation of diffusing adatoms. The distance between islands thus decreases, which, in turn, leads to island impingement at some point during growth. This causes islands to coalesce in order to reduce the surface energy by quickly forming a neck that then grows out before full shape equilibration occurs as schematically depicted in Fig. 2.6 [52, 6, p. 572]. This process is driven by surface diffusion and the time required for its completion, τ_{coal} , assuming two spherical or hemispherical islands with radius R , can be estimated from the classical continuum theory as

$$\tau_{coal} \approx \frac{R^4}{B_{coal}}, \quad (2.2.8)$$

where B_{coal} is a material and temperature dependent coalescence constant [53, 54]. The correctness of the above relationship has however been questioned for far-from-equilibrium conditions when island faceting occurs [55–57]. In that case, facets do not offer any adatom trapping sites, which means that it is more difficult for coalescing islands in an elongated state to equilibrate. Atoms that break free from their bonded sites thus diffuse on the facets where they need to meet another adatom with whom they can nucleate a new layer on the facets. Hence, the rate limiting step for mass transport is nucleation on the facets and not diffusion as in Eq. (2.2.8). In addition, the existence of facets implies that fewer atoms are found on less strong bonding sites such as e.g., edges and kinks, making it less likely for atoms to break loose and

Fig. 2.6. Schematic illustration of two coalescing islands.

become mobile. It should however be pointed out that no deposition was present in Refs. 55–57, which otherwise would act as a source of free adatoms that could increase the probability of nucleation on the facets and thus counteract the impeded mass transport. Regardless of its accuracy, Eq. (2.2.8) is used as a mathematical description of coalescence in Paper 2 in order to be able to account for the increased coalescence time as the island size increases. Another factor that can impede coalescence is the formation of a grain boundary between two impinging islands, since the grain boundary in that case needs to diffuse out in order for coalescence to be completed [54]. Moreover, given that coalescence is completed, a denuded region appears around the newly formed island that enables additional nucleation events to take place. This is referred to as secondary nucleation and gives rise to a bimodal island size distribution.

2.2.4.3 Smoluchowski ripening

Coalescence between islands can also take place even when deposition does not lead to island growth and impingement, as described in the previous section (Sec. 2.2.4.2). This can happen if small islands exhibit sufficient mobility to be able to diffuse on the surface. In that case, a diffusing island can coalesce with another island that is encountered as it migrates on the surface. This process is typically referred to as Smoluchowski ripening. It should however be noted that island diffusion typically is considered to occur for smaller sized islands consisting of less than tens of atoms, with an island diffusivity that normally decreases with increasing island size, even though diffusion of larger islands with hundreds of atoms has been observed [58].

2.2.5 Post-coalescence growth

At some point during growth, as islands grow larger, island coalescence is not completed before a third island impinges on the coalescing cluster since τ_{coal} , in accordance to Eq. (2.2.8), increases with island size. These interconnected islands form elongated structures separated by voids on the substrate surface, and as the majority of islands are in this elongated state the so-called elongation transition is reached. Since island coalescence completion in practice vanishes after this transition, properties such as e.g., grain sizes and surface roughness, are largely determined here [54]. The elongation transition thus denotes the first step towards forming a continuous film. Further deposition causes more and more of these structures to join together, forming networks of interconnected islands. These networks enable free electrons in metallic films to travel longer distances, yielding electrical conductivity. This point is thus commonly referred to as electrical percolation. The interconnected islands characterize a film with void inclusions on the substrate surface. These voids can effectively be treated as atomic islands that are able to reshape in order to minimize surface energy [59], and undergo coalescence via Ostwald and Smoluchowski ripening [60]. Adding more material fills out the voids. This process might be governed by crossing of multiple step edges and leads to the formation of a continuous film.

2.2.6 Growth at non-normal incidences

The most common way to grow thin films is to deposit atoms from the vapor parallel or close to parallel with the substrate surface normal. At far-from-equilibrium conditions this typically leads to a columnar microstructure where columns or grains are separated by grain boundaries. If the flux instead arrives at an angle with respect to the substrate surface normal the initially formed islands shadow the area behind them, preventing atoms from the vapor to be deposited in this region. Atoms are thus preferentially captured by preexisting islands, which also is enhanced by steering of the deposition flux due to attractive forces between deposited atoms and existing islands [61]. This decreases island density and increases the average island size, delaying the onset of coalescence [62]. As growth continues some islands stop growing due to shadowing from islands in front of themselves, creating a porous columnar microstructure with columns tilted towards the vapor flux source as can be seen in Fig. 2.7. In addition to tilted columns, it is also possible to engineer the columnar

Fig. 2.7. Snapshot from a molecular dynamics simulation (see Sec. 4.1) of Cu on Cu deposition at 300 K from an incidence angle of 80° with respect to the substrate surface normal. Shadowed islands that no longer grow are seen at the substrate surface together with columns that are tilted towards the material source. Image courtesy of Dr. Georgios A. Almyras.

structure by rotating the substrate around its normal and/or tilting it relative to the incoming flux. This enables the formation of films that are sculptured into helical [63] and zig-zag [64, 65] patterns, vertical [63, 65] and s-shaped [66] columns, or as combinations thereof [67]. The operational procedure of using a non-normal incidence angle when growing thin films is commonly referred to as oblique angle deposition, glancing angle deposition, off-normal growth or inclined substrate deposition, and finds applications in the areas of e.g., photovoltaic cells, sensors and optics [16, 17].

The resulting tilt angle of the columns depends on the incidence angle of the vapor flux, but it can also be altered by changing film composition [21], spatial distribution of the vapor flux [18–20] or the kinetic growth conditions [16, 68]. The most common way to affect the latter is by varying the substrate temperature. This has been shown to result in columns that grow either closer to [69–71] or further away [68, 72, 73] from the direction of the substrate surface normal as the temperature is increased. The first observation is typically encountered for higher temperatures/diffusivities while the second is seen for lower. However, due to the large variety of deposition conditions and film-substrate combinations in the referenced studies it is difficult to draw any general conclusions on how e.g., diffusion is affecting the structure. Despite the contradicting results the two observations have both been explained on the basis of surface diffusion. The first observation, where columns are observed to grow closer to the substrate surface normal with increasing temperature, is commonly explained via Fick's first law of diffusion, which postulates that diffusion tries to eliminate concentration gradients. This means that an increased surface diffusion causes more adatoms to move from the column tip (high adatom density) towards the shadowed region (low adatom density), and thus position columns closer to the substrate normal [16]. The second observation is explained as a competition between random and biased diffusion [68, 72], the latter induced by conservation of momentum parallel to the substrate surface of newly deposited atoms that arrive at non-normal incidence angles. At lower temperatures the random diffusion of adatoms is considered to be negligible and only the biased diffusion is present. This would push adatoms to the columns shadowed backside, causing them to grow more parallel to the substrate surface normal. As the temperature increases, so does also the random diffusion, which is believed to cancel part of the directional diffusion so that the tilt angle as measured from the substrate surface normal increases. The physical correctness of this second model has however been questioned, where the main critique concerns the existence or not of the biased diffusion [68]. This is due to that the trajectories of low-energy atoms are deflected towards the surface due to attraction [61, 74], as well as that their energy is typically not sufficient for overcoming the diffusion barrier [74, 75]. The threshold in energy is also accompanied by a threshold of the incidence angle since it is only the momentum component parallel to the surface that can give rise to biased diffusion [74, 76]. If the angle, as measured from the substrate surface normal, is small, the parallel momentum component is also small and the probability for biased diffusion would thus be negligible. It is worth noting that the energy barrier for biased diffusion could be

considerably higher than that for random diffusion (E_D) since biased adatoms need to overcome whatever barrier they encounter in order to diffuse, whereas randomly diffusing adatoms can vibrate in the potential well until they find the lowest barrier available [75].

In Paper 3 it is shown that the column tilt angle for Cr increases as the substrate temperature is increased from room temperature. This corresponds to the second observation described above, but instead of the competition between biased and random diffusion the results are suggested to originate from different nucleation characteristics at the various temperatures. This would imply that there are two competing mechanisms present during growth, i.e., nucleation characteristics and adatom diffusion towards shadowed regions. Both of them are surface diffusion driven, but the former relates to diffusion on the substrate and the latter to self-diffusion.

Yet another way to affect the column tilt is to use highly ionized vapor fluxes, as previously has been shown in e.g., Ref. 77. This approach is also systematically investigated in Paper 3, where it is demonstrated that a higher ionization degree can lead to columns positioned closer to the substrate normal if certain nucleation characteristics are present.

2.2.6.1 Predicting column tilt angle

As can be understood from the above discussion there are many factors that can affect the column tilt angle. Despite that, many attempts have been made to correlate the column tilt angle β to the vapor flux incidence angle α , both measured with respect to the substrate surface normal. Probably the most well-known of them is the so called tangent rule

$$\tan \beta = \frac{1}{2} \tan \alpha, \quad (2.2.9)$$

which was found to correlate well with experimental data [78]. Second to that comes the so called cosine rule

$$\beta = \alpha - \arcsin \left(\frac{1 - \cos \alpha}{2} \right), \quad (2.2.10)$$

which is derived from a geometrical model that takes shadowing from neighbouring columns into account [79]. Eqs. (2.2.9) and (2.2.10) constitute the main models used for comparisons with experimental data in the literature, but other models have also been suggested [25, 73, 80–82].

From the results presented in Paper 3, where it was suggested that nucleation characteristics determine column tilt angle, it is possible to set up a simple geometrical model from which a range of accessible column tilt angles can be estimated for conditions of low surface self-diffusivities. The model is based on pre-nucleated hemispherical islands with radius R , separated by a distance L , that are subjected to a collimated vapor flux from an incidence angle α , as depicted in Fig. 2.8.

Fig. 2.8. Illustration of the geometrical model used to predict the column tilt angle depending on the island radius R and island-island separation L .

By going through the calculations (see Appendix A) it is possible to establish a relation for the column tilt angle in the form of $\beta = \beta(\alpha, L/R)$ as

$$\beta = \alpha + \arcsin\left(\frac{\sin(\zeta - \alpha) - 1}{2}\right), \quad (2.2.11)$$

where

$$\zeta = \arcsin\left(\frac{-C_1 + (C_2^2 + 1 - C_1^2)^{\frac{1}{2}}}{1 + C_2^2}\right) \quad (2.2.12)$$

and

$$C_1 = \cos \alpha + \tan \alpha \sin \alpha - \frac{L}{R} \quad (2.2.13a)$$

$$C_2 = \tan \alpha. \quad (2.2.13b)$$

For a certain α it is thus possible to obtain a range of β -values depending on the L/R ratio. At minimum separation, i.e., $L = 2R$, β exhibits its lowest value and at the longest island separation, i.e., when the shadow from the island in front falls at the island-substrate interface, β reaches its largest value. This yields a range of accessible β values for each value of α , which might explain the spread of column tilt angles reported in the literature for cases of low surface self-diffusivities (see e.g., Ref. 68). The results from Eq. (2.2.11) are plotted in Fig. 2.9 for α in the range $0 \leq \alpha \leq 85^\circ$ together with the tangent (Eq. (2.2.9)) and cosine (Eq. (2.2.10)) rules for comparison. It should be noted that as $\alpha \rightarrow 90^\circ$ for islands positioned just next to each other ($L = 2R$), $\beta \rightarrow 0^\circ$ due to the fact that the only part that is not shadowed at these conditions is an infinitesimal region at the very top of the islands. The pre-nucleated islands in the model are thus not sufficient to give a correct description of the growth at these conditions. However, for the extreme shadowing that would be active as $\alpha \rightarrow 90^\circ$, islands would not be expected to nucleate just next to each other, i.e., in reality $L \neq 2R$.

Fig. 2.9. Range of accessible column tilt angles, β , as function of vapor flux incidence angle, α , calculated by Eq. (2.2.11). The tangent (Eq. (2.2.9)) and cosine (Eq. (2.2.10)) rules are also included for comparison.

2.2.6.2 Biaxial alignment

In addition to control the columnar growth direction when growing at non-normal incidence angles it is also, in some cases, possible to obtain films where the grains are crystallographically aligned with each other, both out-of-plane and in-plane. Films with this type of biaxial alignment typically exhibit small miss-orientations between grains that lead to low-energy grain boundaries and a microstructure similar to that of single crystals. They are thus applied as cost-effective large area buffer layers for superconducting [25, 26] and semiconducting [27–29] films.

In order to enable formation of a biaxial alignment, growth needs to take place at kinetically limited conditions where only surface diffusion is active [24]. At these conditions, islands nucleate with random out-of-plane and in-plane alignments[§], which is the starting point for a competitive growth process between differently out-of-plane oriented islands. This is caused by a disparity in adatom diffusivity on top of islands. Islands that expose the surface with the lowest diffusivity offer the longest adatom residence time, and thus an increased probability for adatom incorporation [24, 83–85]. Those islands thus trap more adatoms and hence grow faster, which further leads to protruding islands that capture even more atoms directly from the deposition flux [85]. This means that low diffusivity islands expand, get bound by high diffusivity facets, and eventually overgrow all other islands such that a pre-

[§]For this to be true no epitaxial relationship between film and substrate can be present. If that would be the case the alignments would instead be determined by the substrate.

ferred out-of-plane orientation develops. For vapor fluxes arriving along or close to the substrate surface normal, this means that a uniaxial alignment is generated since the in-plane alignment in that case is unaffected by the overgrowth process.

In order for the preferred in-plane alignment to develop deposition needs, in addition to the kinetically limited growth conditions, to be carried out at a non-normal incidence. As explained in Sec. 2.2.6 this can lead to a directional flux of diffusing adatoms due to conservation of momentum parallel to the substrate surface. In addition, there is also a directional flux of atoms from the vapor that can be directly captured by the growing grains. In the literature the former flux is believed to be the most important of the two in order to generate an in-plane alignment [24]. Based on this flux, a model has been proposed to explain the development of the in-plane alignment in films grown at non-normal incidence angles [24]. The model accounts for the capture cross section, also known as the capture length since it in this case refers to diffusing adatoms, that differently in-plane oriented grains exhibit. Assuming a single diffusion direction, the in-plane alignment that offers the longest capture length traps more adatoms and thus overgrows all other alignments as schematically illustrated in Fig. 2.10 for [001] out-of-plane oriented islands with {100} facets. Note that only islands with the final out-of-plane orientation are considered in the description, islands with different out-of-plane orientations that later are overgrown are not included. In order to better replicate the proposed model, all islands should thus grow with the same out-of-plane orientation already from the very early stages of growth while still remaining an initial random in-plane alignment. This is realized in Paper 4 by employing a uniaxial buffer layer on which the biaxially aligned top-layer is grown epitaxially. Despite this approximation, the model is typically found to be in good agreement with experimental results and capable of predicting the resulting in-plane alignment of many materials [24, 86, 87]. However, there is a discrepancy for some materials where a double in-plane alignment is predicted by the model, but only a single one is observed experimentally. Prior to this thesis, there has only been one experimental report of double in-plane alignment for AlN at an incidence angle of 45° , which for larger incidence angles changed into a single one [88].

As discussed in Sec. 2.2.6, a threshold energy and a threshold angle exist for biased diffusion to be active. Adatoms thus need overcome these threshold values if the biased diffusion is to be active and hence be able to be the decisive mechanism for generating the in-plane alignment. One could argue that a typical average energy of sputter[¶] deposited species on the order of 5 – 10 eV [6, p. 555] is enough for a sufficient amount of adatoms to exhibit a biased diffusion. However, biaxial alignment has also been shown for films prepared by evaporation [89–92] where the average energy typically is on the order of 0.1 eV [6, p. 555]. In that case, no biased diffusion

[¶]Sputtering is explained more in Chap. 3, but here it is enough to know that it is a technique for thin film deposition that is often utilized for the deposition of biaxially aligned thin films. In relation to the average energy referenced, it should also be pointed out that the most probable energy is ~ 2 eV [6, p. 260].

Fig. 2.10. Schematic illustration of the proposed model for the development of the in-plane alignment of [001] out-of-plane oriented islands with {100} facets supported on a substrate. The figure shows a top-view.

would in practice be expected at any incidence angles [74–76]. It could thus be possible that an additional or a different mechanism is involved in the formation of the in-plane alignment.

2.2.7 A note on stress

Stresses commonly develop in thin films as they grow. They can be generated from, e.g., lattice mismatch between substrate and film, point defects in the crystal lattice, and attraction or repulsion of adjacent grains over grain boundaries. Stresses also arise during the growth evolution of Volmer-Weber thin films where a compressive-tensile-compressive behaviour typically is observed for materials exhibiting high diffusivity (like e.g., Ag on SiO₂ as investigated in Papers 1 and 2) [93]. The initial compressive stress corresponds to island nucleation and growth, while the subsequent change into tensile stress is caused by attractive forces between coalescing islands [93]. A continuous film is then formed at the point where the stress changes and once again turns into a compressive state [94], caused by grain boundary densification [95–98]. This point was employed in Paper 1 as a way to denote the formation of a continuous Ag film.

2.3 Alloying

Sometimes the properties offered by the single elements are not enough for what is desired. It is then possible to combine two or more elements into an alloy¹¹. His-

¹¹ An alloy is defined in such a way that at least one of the elements is a metal.

torically, alloying has been performed by humans for thousands of years and has also proven to be an essential part in the development of the human civilization. For example, during the Bronze age Cu was alloyed with other metals like Sn to form bronze or Zn to form brass, in order to increase the hardness of pure Cu [1, pp. 66-67]. Fabrication of these alloys was achieved by casting, which means that thermodynamics mainly determine structure formation. At far-from-equilibrium conditions, kinetics can however hinder the formation of the thermodynamically most stable structure and instead form metastable structures. This is discussed below for the fully miscible and the fully immiscible systems that both have been studied in this thesis (Papers 5 and 6).

2.3.1 Miscible and immiscible systems

From a thermodynamic point of view the propensity or not for intermixing between the different elements in an alloy is determined by Gibbs free energy of mixing, ΔG_{mix} . For an alloy with negative ΔG_{mix} , spontaneous intermixing is favored and the system is miscible. In the opposite case of a positive value, there is instead a thermodynamic driving force for phase separation. To predict solubility ΔG_{mix} can be calculated using its relation to the mixing enthalpy ΔH_{mix} and the mixing entropy ΔS_{mix} as [99, p. 13]

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}. \quad (2.3.1)$$

As a first approximation T is commonly set to zero, meaning that ΔS_{mix} is omitted from the calculations and solubility is based only on ΔH_{mix} . This might seem like a crude approximation, but it is for many systems sufficient [100]. For example, Ag-Ni alloys exhibit a positive ΔH_{mix} at $T = 0$ K that is dominating even at higher temperatures in the liquid state where the elements still are immiscible. For other systems like e.g., Ag-Cu a positive ΔH_{mix} is dominating at lower temperatures where the two elements are immiscible. However, at higher temperatures in the liquid state the contribution from ΔS_{mix} takes over such that ΔG_{mix} turns negative and the elements become miscible.

For far-from-equilibrium conditions, the effect of kinetics can be exemplified by considering a miscible melt of an otherwise immiscible system that is allowed to cool down. At low cooling rates, the diffusion distance for atoms is sufficiently long in order to reach the equilibrium, phase separated, structure. Increasing the cooling rate yields a shorter effective diffusion distance and hence a less phase separated structure. If the melt instead is quenched, i.e., rapidly cooled, atoms are in practice kinetically frozen at their current positions and a metastable structure is formed. For the case of immiscible binary metal alloys (e.g., Ag-Cu) the latter metastable structure is typically found to be an inhomogeneous crystalline solid solution, in the sense that preferential clustering of the single elements occurs on the nanometer length scale [100]. In addition to the solid solution-like structure, amorphous** alloys can

**Amorphous refers to lack of long range order, but short range ordering or clustering has been shown [101].

also form by further lowering the degree of diffusivity [100, 102]. For a miscible system (e.g., Ag-Au) grown at far-from-equilibrium conditions the situation is opposite to that described for the immiscible system. In that case, the driving force is as previously stated towards spontaneous intermixing, and kinetics could only act as a barrier for formation of a solid solution if the constituents are predefined in a decomposed state.

As can be understood from the above discussion the effective diffusion distance covered by the atoms determines the obtained structure. This is typically a somewhat more demanding quantity to describe atomistically since on top of the surface self-diffusion discussed in Sec. 2.2.1, diffusion can also occur on top of other elements or a mixture of elements that significantly can alter the activation energy barriers (see e.g., Ref. 38, pp. 332-341). In an attempt to quantify these barriers experimentally during vapor deposition at far-from-equilibrium conditions, they have instead been averaged into a single effective adatom surface diffusion barrier [103].

The vapor flux used to supply growing thin films with atoms can be generated in different ways. In physical vapor deposition (PVD), this is achieved by vaporizing a solid source material by physical means, typically in a vacuum environment. The most straightforward way to do this is to supply thermal energy as heat until the source material starts to evaporate. Another way is to employ momentum transfer by means of energetic ions that bombard and eject atoms from a solid source material—referred to as target—into the vapor phase. This process is known as sputtering and is usually associated with the use of a plasma.

3.1 Basic plasma physics

A plasma can be described as a quasi-neutral, ionized gas that consists of neutral atoms, ions and electrons [104, p. 3]. As it is confined within a vacuum chamber, the quasi neutrality, i.e., that electron and ion densities are the same when averaged over a large volume, is no longer valid where the plasma gets in contact with a conductive surface. This is due to a higher electron velocity that causes more frequent losses of electrons to the surface, resulting in a positive net charge density in a region close to the surface that is referred to as sheath. After crossing the sheath, the bulk plasma is entered. Due to the positive net charge in the sheath, the plasma exhibits a positive potential (plasma potential, V_p) with respect to the conductive surface, as illustrated in Fig. 3.1. For plasma based sputtering processes the value of V_p is typically around 1 – 5 V [105–108]. A similar situation arises if a conducting object, shielded from other potentials, is immersed into a plasma. In that case, the faster electrons start to build up a negative charge of the object. This means that ions are attracted towards and electrons are repelled away from the object. As the net current is zero, no further charging takes place, yielding a negative potential known as floating potential, V_f

Fig. 3.1. Typical potential of a plasma used in a sputtering process. An external potential is applied to the cathode and the anode is grounded.

(see Fig. 3.1). This quantity typically takes values between -10 and -20 V [105, 109–111].

3.2 Magnetron sputtering

In order to deposit thin films by plasma based processes an inert gas, typically Ar, is let into a vacuum chamber after which a negative potential is applied to the target (cathode). This causes free electrons[†] close to the cathode to be accelerated towards the anode. On their way, they can undergo inelastic collisions with neutral Ar atoms, causing impact ionization[‡] that generates more free electrons. All these free electrons give rise to an electron avalanche that is accelerated towards the anode, creating even more ionization events. This leads to breakdown of the gas and creation of a plasma. At the same time, the generated ions are attracted and accelerated towards the cathode. As they collide with the target, momentum is transferred to atoms in the surface region that, through collision cascades, can be ejected into the vapor phase, i.e., be sputtered. This process can also create secondary electrons that help to sustain the plasma.

The efficiency of the sputtering process can further be increased by confining the plasma in the close vicinity of the target. This can be achieved by applying magnets

[†]Some free electrons are always present in a gas, e.g., caused by background radiation.

[‡]Other important ionization events in the framework of this thesis are charge exchange ionization and penning ionization, where an excited atom transfers energy to a neutral atom that leads to ionization.

Fig. 3.2. Schematic cross-sectional view of a magnetron sputtering source.

behind the target as illustrated in Fig. 3.2. By doing so, charged particles experience the Lorentz force, $\vec{F}_L$, given as [104, p. 21]

$$\vec{F}_L = q(\vec{E} + \vec{v} \times \vec{B}), \quad (3.2.1)$$

where q is the particle charge, $\vec{E}$ the electric field, $\vec{v}$ the velocity of the particle and $\vec{B}$ the magnetic field. The addition of a $\vec{B}$ field traps electrons close to the cathode. Ions, on the other hand, are only weakly affected by $\vec{F}_L$ due to their larger mass [6, p. 46], but are nonetheless confined in the vicinity of the target region in order to maintain the quasi-neutrality of the plasma. The plasma based deposition technique direct current magnetron sputtering (DCMS) utilizes this setup together with a constant power applied to the cathode to generate a continuous supply of atoms to the substrate. The vapor flux created by DCMS consists mainly of neutral atoms (only a few percent of the flux are typically ionized [112]) due to low plasma densities ($< \sim 10^{16} \text{ m}^{-3}$ [113, 114]) that yield low probabilities for ionization of sputtered atoms.

3.3 High power impulse magnetron sputtering

Higher ionization degrees of the sputtered species are often desired since energies and trajectories of ions can be controlled to a much higher degree than the corresponding quantities for neutrals. One way to manipulate ions is to simply apply a negative potential to the substrate causing a potential difference between bulk

plasma and substrate that accelerates ions towards the growing film[§]. This can change the angular distribution of the flux and trigger surface processes that enable growth of dense and smooth films, even on complex-shaped substrates. The need for higher ionization degrees during magnetron sputtering lead to the emergence of the deposition technique high power impulse magnetron sputtering (HiPIMS) [113–119]. In HiPIMS, the power is delivered to the cathode in well-defined pulses with low duty cycles ($< 10\%$) and frequencies lower than ~ 10 kHz, which allows heat to be dissipated between pulses to avoid target melting. This makes it possible to obtain high plasma densities ($\sim 10^{19} \text{ m}^{-3}$ [120]) with ionization degrees of the sputtered material that for some conditions can reach close to 100 % [121]. The ionized species do also normally exhibit higher energies (tens of eV) than neutrals (a few eV). This has been suggested to be due to temporal variations of the space charge within the plasma, which leads to local electric fields that cause acceleration of charged species [122, 123]. The pulsed character of this deposition process is also shown to result in a pulsed deposition flux with a frequency corresponding to that applied to the cathode in Paper 1. The width of each vapor pulse is, however, slightly longer than the active part of the pulse due to scattering of the sputtered species in the gas phase [124, 125].

Despite the advantages offered by the high ionization degree, it is also typically considered to be one of the main drawbacks of HiPIMS as compared to conventional DCMS. This is due to that part of the ionized species might not possess sufficient energy to overcome the cathode sheath potential and are thus attracted back to the target. The back-attraction causes sputtering, that due to a normally lower self-sputter yield[¶] as compared to the sputter yield of the inert process gas [114], results in a loss of deposition rate. In addition, the sputter yield exhibits a square-root dependence with the powers typically applied in DCMS and HiPIMS [126]. This means that a lower average deposition rate is expected for the higher powers utilized in the HiPIMS pulses as compared to in DCMS when used with the same time averaged power [127].

3.4 Modulated impulse magnetron sputtering interplay

The high degree of ionization in HiPIMS gives additional kinetic handles to control the growth as discussed in the previous section (see Sec. 3.3), but for the case of multicomponent materials properties are in addition also determined by the atomic arrangement of the film forming species. A common way to alter the atomic arrangement is by changing the arrival pattern of the vapor flux by using mechanical shutters in front of the targets that sequentially open and close. This leads to a modulated flux that is widely employed to grow alternating layers of materials in the form of superlattice structures. Using shutters do, however, restrict the time scale of the

[§]The same is also valid for electrically floating or even grounded substrates due to the positive potential of the plasma, V_p .

[¶]Sputter yield is a measure on the average number of sputtered atoms per incident ion and depends on the chemical elements of target and ion, as well as the energy and incidence angle of the ion.

Fig. 3.3. Schematic illustration of the deposition process modulated impulse magnetron sputtering interplay (MIMSI). In this process multiple power supplies are used to generate electrical pulse trains that sequentially activate different magnetrons. This yields a modulated vapor flux that can be controlled by altering the characteristics of the pulses and the pulse trains.

modulation, and thus also the resolution of the modulation, to the time required to physically move the shutters (typically on the order of 100s of ms to a few s). In order to circumvent this restriction and still maintain the additional control offered by the pulsed vapor flux a new deposition technique named Modulated Impulse Magnetron Sputtering Interplay (MIMSI) [128] has been developed during the course of this thesis. MIMSI utilizes multiple power supplies to generate synchronized bursts of pulses that trigger separate magnetron sources as schematically illustrated in Fig. 3.3. Each individual pulse exhibits the same characteristics as its HiPIMS counterpart, which means that the time scale of the flux modulation can be controlled on the μs time scale. This, in combination with the fact that the typical deposition rate per pulse is in the range $10^{-4} - 10^{-2}$ monolayers, mean that the arrival pattern of the vapor flux and the amount of material deposited can be controlled with a very high resolution by simply changing the number of pulses that are supplied in each pulse train.

MIMSI is employed in Papers 5 and 6 to determine the applicability of using this technique in order to manipulate the atomic arrangement of miscible (Ag-Au) and immiscible (Ag-Cu) model systems as well as to determine the decisive structure forming processes within these systems.

Computer simulations are today utilized in a wide range of areas, such as finance, military and science, to predict or understand outcomes or strategies. In the field of materials science, simulations can be employed to bridge the gap between atomistic processes and macroscopic properties in order to explain or anticipate how they correlate with each other. For the sake of this thesis, where the area of interest is thin film growth, it is desired to be able to perform simulations of the growth process in real time. This is here accomplished by using two different methods briefly explained below.

4.1 Molecular dynamics

Molecular dynamics (MD) simulations are used to gain insight in the dynamical evolution of a system of interacting atoms or molecules. In the classical treatment this is achieved by considering Newton's equations of motion and numerically solve the second law of motion

$$\vec{F}_i = m_i \frac{d^2 \vec{r}_i}{dt^2} \quad (4.1.1)$$

for all particles in the system. In Eq. (4.1.1), $\vec{F}_i$ is the force exerted on particle i with mass m_i and position $\vec{r}_i$, and t denotes time. $\vec{F}_i$ can further be determined from the interatomic potential U as

$$\vec{F}_i = -\nabla_{\vec{r}_i} U, \quad (4.1.2)$$

where $\vec{r}_{ij}$ denotes the distance between particles i and j . In principle, this means that if U is accurately known it is possible to calculate the evolution of positions ($\vec{r}_i$), velocities ($d\vec{r}_i/dt$) and accelerations ($d^2\vec{r}_i/dt^2$) for the particles as based on their relative positions. In reality, however, U is a complex quantity arising from atomic interactions, and hence needs to be approximated by the use of mathematical models.

In this thesis two different interatomic potentials are employed, an Ag-Cu Embedded Atom Method (EAM) potential [129] and an Ag-Au-Cu Finnis-Sinclair potential [130] in Papers 5 and 6, respectively, to describe the interactions between Ag-Cu and Ag-Au during growth. The simulations are executed using LAMMPS software [131] and the results are visualized in Ovito [132].

Apart from the importance of an accurate description of U , MD simulations are limited by the fact that the time step needs to be sufficiently short, i.e., in the fs-range, in order to resolve atomic vibrations [133, p. 2]. With the computational resources available today, this limits the total simulation time typically to the ns-range. For the case of thin film deposition, this means that arrival rates much higher than those used experimentally are employed, which, in turn, increases island densities (cf. Eq. (2.2.3)) and shortens relaxation times for diffusion and sintering processes. Nonetheless, MD simulations are a powerful tool to study the atomistic processes present during, and responsible for, thin film formation.

4.2 Kinetic Monte Carlo

Kinetic Monte Carlo (KMC) simulations circumvent the limitations of total simulation time in MD by employing a stochastic approach instead of a deterministic. This is accomplished by assigning probabilities to the different events that can take place in the simulations as based on the rates at which they occur. For adatom diffusion this means that it is only the transition, in itself, between two sites that is considered, not an adatom's full motion between sites as in MD. This enables a dramatic increase in total simulation time.

During each step in the KMC simulations, a possible event is chosen randomly as based on its probability before being carried out. Any implications arising from the executed event is then analyzed before the time is increased and a new random event is chosen. For the film growth simulations in Paper 2, this means that one of two main events can occur during each time step; addition of a new adatom through deposition or movement of an already existing adatom by diffusion. The real time is thus determined by the arrival rate of new adatoms and the adatom diffusivity (set by Eq. (2.2.2)). If a diffusion event is chosen, the selected adatom moves randomly to any of the four nearest-neighbour positions on a squared substrate lattice with periodic boundary conditions. The probability of doing so is equal in all directions, i.e., E_D is the same independent of diffusion direction. At its new position the adatom can form a new nucleus if an adjacent adatom is present (assuming $i^* = 1$), get incorporated into an existing island or simply stay at rest. Similarly, if an atom is deposited it can get incorporated in an existing island by direct capture, create a new nucleus or become a free adatom. For impinging islands, the coalescence time is calculated in accordance to Eq. (2.2.8) and if this time is reached, a new island is formed from the coalescing islands. This procedure is then repeated until the end of the simulation.

Throughout the simulations used in Paper 2, the number of islands on the substrate surface and their size (number of atoms) as well as the number of nucleation, island impingement and completed coalescence events are accumulated to characterize the growth process. The number of islands is then used to extract a ratio between the total number of islands and the total number of clusters[†]. As this ratio equals two, each cluster consists, on average, of two islands, which is taken to be equivalent to elongated island structures. This point during growth is chosen as the elongation transition [134]. The thickness at which this happens is used as a comparative measure between different simulations to study scaling behaviours for different growth processes. In addition, the number of events are used to calculate rates of the corresponding processes in order to determine the role of island nucleation, island growth and island coalescence on the growth evolution.

[†]A cluster consists of interconnected islands, where the smallest sized cluster is defined as a single island.

5.1 Mass spectrometry

Mass spectrometry is an analysis technique capable of measuring atomic masses and energies. It is utilized in thin film processes to provide quantitative information of plasma chemistry.

An extraction probe with a small orifice (tens to hundreds of μm in diameter) is immersed into the plasma through which gas atoms and ions may enter the mass spectrometer. The incoming species are then filtered depending on their energy and mass-to-charge ratio using electric and magnetic fields before being detected. This implies that neutral species first need to be ionized in order to be studied. Commonly, this is accomplished by employing a heated filament that ejects electrons, causing ionization upon impact. Different types of filters exist and in this thesis a Bessel box is employed as energy filter. It uses electrodes with applied potentials to only allow ions with a specific energy to pass. As mass filter, a quadrupole is utilized. It employs four parallel metal rods, onto which a constant as well as a time-varying potential is applied. Depending on the potentials, only ions with a certain mass-to-charge ratio are able to travel through the filter without colliding with the rods and finally reach the detector. This is the setup utilized in Paper 1 to study the pulsed nature of the ionized deposition flux generated in the HiPIMS process (see Sec. 3.3) as well as the corresponding ion energies.

5.2 Quartz crystal microbalance

A quartz crystal microbalance (QCM) is an instrument that is capable of detecting a small addition or removal of mass. Thanks to its ease of use it is widely employed to monitor deposition rates during thin film growth.

The QCM is based on the piezoelectric effect where an applied mechanical strain generates an electric field across a piezoelectric material. In the same way, applying an electric field causes a mechanical strain that restores as the field is removed, i.e., an elastic deformation. By applying an alternating potential, the crystal starts to oscillate and a standing wave can be generated. The corresponding resonance frequency of the wave is highly sensitive to changes in the thickness of the crystal, which means that if an additional layer is deposited on top of the crystal the resonance frequency shifts. Assuming a uniform and rigid layer, the shift of the resonance frequency can be directly correlated to the mass change per unit area via the Sauerbrey equation [135]. With knowledge of film density the deposition rate can be extracted. This is done in Paper 3 for one deposition set to ensure the same deposition rate for all deposition conditions.

5.3 Spectroscopic ellipsometry

Spectroscopic ellipsometry is a surface sensitive optical characterization technique that measures changes in the polarization state of light that is reflected from a material. It is typically used to provide optical properties and film thicknesses, but can also be utilized to determine other material properties, such as surface and interface roughness, electrical resistivity and chemical composition. A main attribute of this technique, for the sake of the work conducted in this thesis, is its capability of being used *in situ* to acquire real time measurements during thin film growth.

In spectroscopic ellipsometry, a sample is illuminated by polarized light[†] at multiple energies, ω , in the visible or close to the visible spectrum (see Fig. 5.1). As the electromagnetic waves interact with the sample they can induce dipole moments and yield electron transitions. This optical response of the material is characterized by the complex dielectric function, $\tilde{\epsilon} = \tilde{\epsilon}(\omega)$, which normally is separated into its real and imaginary parts as

$$\tilde{\epsilon} = \epsilon_1 + i\epsilon_2. \quad (5.3.1)$$

ϵ_1 and ϵ_2 correspond to light dispersion and absorption, respectively, and are correlated with each other through the Kramers-Kronig relations[‡] [136, p. 179]. $\tilde{\epsilon}$ is also related to the complex index of refraction $\tilde{n}$ that describes how light is affected by the interaction with matter as $\tilde{n} = n + i\kappa = \sqrt{\tilde{\epsilon}}$ [137, p. 430]. n is here the refractive index and κ is an extinction coefficient describing light attenuation. For a bulk material, $\tilde{n}$ is related to the Fresnel reflection coefficients, r_p and r_s , [138, p. 280] where p and s refer to the planes that are parallel and perpendicular to the plane of incidence, respectively (see Fig. 5.1). They are the normalized electric field components with respect to the incident electric field in the p and s planes, respectively, and thus a

[†]Polarized light is light where the electric field components only propagate in specific orientations in space. Typically, linearly polarized light is employed, but any kind of polarization can be utilized as long as it is known.

[‡]The Kramers-Kronig relations are mathematical relationships that correlate the real and imaginary part of a complex function. I.e., if one part is known the other can be calculated.

Fig. 5.1. Setup for spectroscopic ellipsometry measurements where linearly polarized light illuminates a sample and is reflected as elliptically polarized.

measure on the change of polarization for each direction. The latter typically happens differently in the p and s directions causing the reflected light to be elliptically polarized.

The ratio of r_p and r_s is called the complex reflectance ratio, ρ , and is the quantity of interest in reflection spectroscopic ellipsometry measurements. It is related to the experimentally determined ellipsometric angles Ψ and Δ by the relationship [139]

$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}. \quad (5.3.2)$$

With ρ it is then possible to obtain $\tilde{\epsilon}$ as [138, p. 280]

$$\tilde{\epsilon}(\omega) = \tilde{n}_0^2 \sin^2 \theta \left(1 + \left(\frac{1 - \rho(\omega)}{1 + \rho(\omega)} \right)^2 \tan^2 \theta \right), \quad (5.3.3)$$

where $\tilde{n}_0$ is the complex index of refraction of the sample's ambient (for vacuum $\tilde{n}_0 = 1$) and θ the incidence angle of the light with respect to the sample surface normal. The above equation is, however, only valid for bulk materials where transmitted light is totally absorbed within the material. This is not the case for thin films grown on a substrate where part of the light is reflected back at the film-substrate interface. The latter causes light to once again travel through the film before reaching its surface where both reflection and transmission occur. Due to these multiple reflections, the optical response of the three phase system (ambient-film-substrate, denoted as medium 0-1-2) is instead determined by the total Fresnel reflection coefficients, R_p and R_s , given as [138, p. 282]

$$R_p = \frac{r_{01p} + r_{12p} e^{i2\tilde{\xi}}}{1 + r_{01p} r_{12p} e^{i2\tilde{\xi}}} \quad (5.3.4a)$$

$$R_s = \frac{r_{01s} + r_{12s} e^{i2\tilde{\xi}}}{1 + r_{01s} r_{12s} e^{i2\tilde{\xi}}}. \quad (5.3.4b)$$

Here, r_{01j} and r_{12j} are the Fresnel reflection coefficients for the ambient-film (medium 0 to 1) and the film-substrate (medium 1 to 2) interface, respectively, and ξ the phase angle that is defined as [138, p. 282]

$$\xi = \frac{2\pi d}{\lambda} \sqrt{\tilde{n}_1^2 - n_0^2 \sin^2 \theta}. \quad (5.3.5)$$

In the above equation, d is the film thickness and λ the wavelength of the light in vacuum. The expression of ρ thus changes into

$$\rho = \frac{R_p}{R_s}, \quad (5.3.6)$$

which infer that ρ now carries information about the entire three-phase system, i.e., the corresponding complex dielectric functions as well as d . This means that a combined complex dielectric function for the whole system, known as pseudo-dielectric function $\langle \tilde{\epsilon}(\omega) \rangle$, is obtained when using Eq. (5.3.3).

5.3.1 Optical models of metals

Spectroscopic ellipsometry is an indirect characterization technique in the sense that physical properties are determined by modelling the sample under investigation. In this section the models used to represent the optical response of the film during this thesis work are presented.

5.3.1.1 Lorentz oscillator

The Lorentz oscillator model describes the interaction between electric fields and atoms by considering the motion of an electron bound to a positive ion positioned in an external electric field[§], $\vec{E}(t) = \vec{E}_0 e^{-i\omega t}$. The electric field exerts a force on the electrons causing them to be displaced from their equilibrium positions as $\vec{r}(t) = \vec{r}_0 e^{-i\omega t}$. This situation can be described classically by the equation of motion for a single electron with charge e and mass m_e when it is considered to be attached to a fixed ion (due to its heavier mass) through a damped spring, according to [139, 136, p. 43]

$$m_e \frac{d^2 \vec{r}}{dt^2} = -m_e \Gamma \frac{d\vec{r}}{dt} - m_e \omega_0^2 \vec{r} - e \vec{E}(t). \quad (5.3.7)$$

In the equation, ω_0 is the resonance frequency of the electron oscillations, and Γ is a damping constant (also referred to as broadening). The latter accounts for energy losses that for solids are due to internal scattering [136, p. 43]. Eq. (5.3.7) can be solved by taking its Fourier transform, which after rearranging yields the displace-

[§]To be fully accurate one should consider the average local electric field, $\vec{E}_{loc}$, that displaces an electron. However, in the case of free electron metals as studied in this thesis it is sufficient to assume that $\vec{E}_{loc} = \vec{E}$ to capture all essential optical features [140, p. 44].

ment of the electron as

$$\vec{r}(\omega) = -\frac{e\vec{E}(\omega)}{m_e(\omega_0^2 - \omega^2 - i\Gamma\omega)}. \quad (5.3.8)$$

The displacement induces a dipole moment according to $\vec{p} = -e\vec{r}$ from which the total polarization per unit volume $\vec{P}$ is obtained by multiplying with the electron density N_e

$$\vec{P} = -eN_e\vec{r}. \quad (5.3.9)$$

$\vec{P}$ is in turn related to the electric displacement field, $\vec{D}$, and $\vec{E}$ as

$$\vec{D} \equiv \tilde{\epsilon}\epsilon_0\vec{E} = \epsilon_0\vec{E} + \vec{P}, \quad (5.3.10)$$

where ϵ_0 is the permittivity of free space. By combining Eqs. (5.3.8), (5.3.9) and (5.3.10), and rearranging, $\tilde{\epsilon}$ can be identified as

$$\tilde{\epsilon}(\omega) = 1 + \frac{e^2N_e}{\epsilon_0m_e} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega}. \quad (5.3.11)$$

In real materials bound electrons can also be excited and undergo interband transitions that commonly occur at higher energies and for the case of Ag starts at 3.8 eV [141]. These excitations do also contribute to $\tilde{\epsilon}$ and can e.g., be modelled with additional oscillators. However, some of them typically occur above the experimentally accessible energy range and their contribution is in that case summarized in the real valued parameter ϵ_∞ that is added to Eq. (5.3.11). The final expression for the Lorentz oscillator is thus

$$\tilde{\epsilon}(\omega) = \epsilon_\infty + \frac{e^2N_e}{\epsilon_0m_e} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega}. \quad (5.3.12)$$

The applicability of using a Lorentz oscillator to describe the optical response of thin films can be understood by considering a non-continuous film consisting of separated atomic islands (with metallic behaviour) present on a non-conducting substrate surface. In that case, an island can be considered to consist of fixed positively charged ions with freely moving and evenly spread conduction electrons as illustrated in Fig. 5.2 (a). Illuminating the island with light causes the electric field of the light to induce displacement and accumulation of the electrons on one side of the island as depicted in Fig. 5.2 (b). This creates an electric dipole in the island that gives rise to an electric field ($\vec{E}_{res}$ in Fig. 5.2 (b)) opposite to that applied, which generates a restoring force on the electrons. For the case of a static applied field that is removed at some point, the restoring force would cause the electrons to collectively oscillate over the island at a resonance frequency (corresponding to ω_0 in Eq. (5.3.12)). Ideally, the oscillations should go on, but due to damping from the ions and the island surface they cease. These collective electron oscillations, that are known as localized surface

Fig. 5.2. Schematics of a metallic island (a) without and (b) with light interaction. In (b) electrons move opposite to the applied electric field, $\vec{E}_{light}$, which, in turn, creates a restoring field inside the island, $\vec{E}_{res}$.

plasmon resonances [9], are thus similar to a harmonic oscillator with damping and, hence, well described by the Lorentz oscillator.

For electromagnetic waves the electric field is however not static, instead it is alternating. This produces a time varying force that in turn causes the localized surface plasmon resonances to move with the same frequency as that of the applied field. As the applied frequency matches that of the resonance, the amplitude of the electron oscillations is going to reach its maximum. This further means that the most pronounced light absorption takes place at this frequency, yielding selective absorption. In this thesis, the Lorentz oscillator is applied in Paper 2 to model the optical response of non-continuous Ag films in order to extract the evolution of the resonance frequency, ω_0 . It is then used as input for calculations of the Ag areal coverage using Doremus method (see Sec. 5.3.1.3).

It should be noted that islands that are not well-separated can start to interact with each other causing additional dipoles to emerge. This means that a single Lorentz oscillator is no longer sufficient to describe the optical response of the film. The same is also true for a bimodal size distribution of islands [142] or for islands that are elongated in one direction like nanorods [143].

5.3.1.2 Drude model

For bulk metals the free conduction electrons are essentially unbound and the restoring force can thus be treated as negligible. This means that ω_0 vanishes from Eq. (5.3.12). The Drude equation then follows as [139, 136, p. 53]

$$\tilde{\epsilon}(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} \quad (5.3.13)$$

where the plasma frequency ω_p is introduced as

$$\omega_p = \sqrt{\frac{e^2 N_e}{\epsilon_0 m_e}}. \quad (5.3.14)$$

Fig. 5.3. Resistivity, ρ_{res} , as a function of nominal thickness (amount of deposited material). The point used to determine the continuous film formation is depicted in the figure.

By modelling the optical response of the film using the Drude model it is also possible to calculate the film resistivity ρ_{res} as [139]

$$\rho_{res} = \frac{\Gamma}{\epsilon_0 \omega_p^2}. \quad (5.3.15)$$

This is done for continuous and close to continuous films in Papers 1 and 2 in order to monitor the evolution of ρ_{res} . From the evolution, the transition to a continuous film is extracted as the point where a steady-state value is reached [144], as indicated in Fig. 5.3.

5.3.1.3 Doremus method

In 1966, Doremus [145] developed a method to determine the area fraction, Q , that a non-continuous metal film covers on a substrate depending on the maximum absorption of the film. In the derivation, the film was described as a collection of separated islands embedded in a dielectric medium using the Maxwell-Garnett [146] effective medium approximation[¶]. By considering an analytical expression of the film absorp-

[¶]Effective medium approximations (EMAs) can be used to describe an effective $\tilde{\epsilon}(\omega)$ based on a relation of the different elements' $\tilde{\epsilon}(\omega)$ and their volume fractions. Different models exist where one of the most well-known is the Maxwell-Garnett that assumes well-separated spherical inclusions of a material in a matrix.

tion Doremus found that a maximum occurred when [145]

$$\epsilon_1 = -\frac{(2+Q)n_2^2}{1-Q}. \quad (5.3.16)$$

Here, ϵ_1 is the real part of the bulk complex dielectric function of the island material taken at the maximum absorption energy and n_2 the refractive index of the substrate. This simple relation has been shown to yield excellent agreement with experiments for Q values in the range 19 – 63 % [147].

In Paper 2, Eq. (5.3.16) is utilized to monitor the evolution of Q for Ag films consisting of separated islands. The optical response of the films is modelled by a single Lorentz oscillator (see Sec. 5.3.1.1) where the energy at which maximum absorption occurs is given by ω_0 . In this way, ϵ_1 in Eq. (5.3.16) could be extracted from reference data in Ref. 148 as $\epsilon_1 = \epsilon_1(\omega_0)$.

5.3.1.4 Arwin-Aspnes method

Arwin-Aspnes method is a graphical method that concurrently determines film thickness, d , and $\tilde{\epsilon}$ [149]. The derivation assumes that $\rho = \rho(\tilde{\epsilon}, d)$, i.e., that all other relevant parameters ($\tilde{\epsilon}$ of substrate and ambient as well as energy and incidence angle of the light) are known. An approximate solution can then be found by expanding $\rho(\tilde{\epsilon}, d)$ to the first order around a hypothetical thickness $\langle d \rangle$, which is close to d , according to

$$\rho(\tilde{\epsilon}, d) = \rho(\langle \tilde{\epsilon} \rangle, \langle d \rangle) + \frac{\partial \rho}{\partial d}(d - \langle d \rangle) + \frac{\partial \rho}{\partial \tilde{\epsilon}}(\tilde{\epsilon} - \langle \tilde{\epsilon} \rangle). \quad (5.3.17)$$

Fig. 5.4. Thickness determination using Arwin-Aspnes method. As can be seen, a thickness of 140 Å minimizes the substrate feature around 1.9 eV.

As is evident from Eq. (5.3.17), $\rho(\tilde{\epsilon}, d) = \rho(\langle \tilde{\epsilon} \rangle, \langle d \rangle)$ if [149]

$$\langle \tilde{\epsilon} \rangle = \tilde{\epsilon} + (d - \langle d \rangle) \frac{\partial \rho / \partial d}{\partial \rho / \partial \tilde{\epsilon}}. \quad (5.3.18)$$

This, in turn, means that if $\langle d \rangle = d$ (i.e., that the guessed hypothetical thickness is correct) it is also valid that $\langle \tilde{\epsilon} \rangle = \tilde{\epsilon}$. Consequently, both d and $\tilde{\epsilon}$ are determined at the same time.

A prerequisite for this method to work is that an optical feature from the substrate is present within the measured ω range. In that case, the feature shows up as an artifact in $\langle \tilde{\epsilon} \rangle$ if $\langle d \rangle$ is not the correct thickness since the last term in Eq. (5.3.18) in that case is nonzero. An example of $\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$ for different $\langle d \rangle$ values of a Ag film is given in Fig. 5.4. As can be seen, a thickness of 140 Å minimizes the influence of the substrate feature around 1.9 eV. Further refinement yields a thickness of 143 Å.

By utilizing Arwin-Aspnes method for *in situ* real time measurements of film growth it is possible to determine the evolution of $\tilde{\epsilon}$, as displayed in Fig. 5.5 for a Ag film grown on SiO₂. The evolution of $\tilde{\epsilon}$ can, in turn, be employed to determine the time (or equivalently the nominal thickness) at which a film first starts to show metallic behaviour. This is accomplished by noting when ϵ_1 becomes negative close to the near infrared region of the spectrum (low energy) [150], which previously has been shown to be in good agreement with *in situ* resistivity measurements [151]. In Fig. 5.5 this corresponds to a film thickness between 100 and 109 Å, which with a refined analysis results in a percolation thickness of 108 Å. This methodology is ap-

Fig. 5.5. Evolution of the complex dielectric function for a growing Ag film as extracted from Arwin-Aspnes method.

plied in Paper 2 to extract percolation thicknesses for Ag films grown on SiO₂. In relation to this, it is worth noting that the absolute value obtained for the percolation thickness depends on the low energy range employed in the measurements. This does however not affect the applicability of studying the scaling behaviour of the percolation thickness as is done in Paper 2.

5.4 Stress measurement by wafer curvature

Stress measurement by wafer curvature is a method that makes it possible to obtain film stresses in real time. The basic principle of the technique is that a stressed film, constrained on a substrate, exerts a force on the substrate that causes it to bend until force equilibrium is reached. The radius of curvature, R , of the bent substrate can then be related to the film stress, σ , through the Stoney equation or a modified Stoney equation depending on type of substrate used. In the case of Si (100), as is used in Paper 1, the modified Stoney equation is given by [152]

$$\sigma d = \frac{Mh^2}{6R}, \quad (5.4.1)$$

where d is the film thickness, M the biaxial modulus of the substrate and h the thickness of the substrate. As seen in Eq. (5.4.1) no specific film properties are required, except for film thickness, or similarly, in the case of real time measurements, deposition rate. Measurements of R can be done in various ways, where the one employed in Paper 1 to determine the formation of continuous Ag films, uses parallel laser beams that are reflected from the substrate surface onto a CCD camera, as illustrated in Fig. 5.6. The curved substrate causes the reflected beams to deflect, which makes it possible to determine R by comparing the spacing between the outgoing beams with the spacing of the reflected beams at the CCD camera.

Fig. 5.6. Principles of a stress measurement by wafer curvature. The incoming laser beams are reflected at different angles due to the curved substrate.

5.5 Electron microscopy

An electron microscope employs an accelerated electron beam to capture an image of an object. It emerged in an attempt to overcome the resolution limit of conventional visible light microscopes (~ 200 nm [153, p. 5]) caused by the long wavelength of visible light ($\sim 400 - 700$ nm). This is to be compared to the much shorter wavelength of an electron, whose actual value depends on energy and can e.g., be calculated to 2.5 pm for an electron accelerated by 200 kV. It is worth noting that this wavelength is much shorter than the diameter of an atom and hence electron microscopes are not wavelength-limited, but rather limited by imperfect electron lenses [153, p. 91]. Electron microscopes are commonly used in materials science when structure and elemental information is needed, and during the course of this thesis work different types have been used. An introduction to them are given below.

5.5.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is a widely used imaging technique for thin films owing to its high resolution capabilities (nanometer scale is possible [154, p. 2]) together with easy handling and data interpretation. With the use of SEM, it is possible to obtain microstructural information about the film.

In order to obtain a micrograph, an electron beam is accelerated (typically by a few to tens of kV) and focused to a small spot on the surface of the specimen. As the electrons impinge on the surface, some of them are backscattered, while others can give rise to secondary electrons. By raster scanning the electron beam across an area of interest and at the same time detecting the intensity of either backscattered or secondary electrons, an image is formed in a pixel-by-pixel fashion. The backscattered electrons are caused by elastic collisions between incoming electrons and atoms in the sample, meaning that an incoming electron's trajectory changes due to attraction from the atoms' positively charged cores. As a consequence, electrons backscatter more for heavier atoms, generating elemental contrast in the micrograph. On the other hand, secondary electrons are caused by inelastic scattering and since their energies are comparatively low, they originate from the near surface region. This means that the signal from the secondary electrons is surface sensitive and mainly carries information originating from the surface structure.

In Paper 3, SEM is used as characterization technique to measure tilt angles of the columnar microstructure in off-normally grown films as well as the corresponding film thickness by investigating cross-sectional samples.

5.5.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is an imaging method that is capable of achieving a resolution below 1 Å for suitable specimens [153, p. 6], making it possible to obtain structural and chemical information at the atomic scale.

During TEM operation, a specimen is illuminated by a coherent electron beam that is accelerated to high energy (typically $\sim 100 - 300$ keV). The transmitted electrons are then projected onto a viewing screen or camera to render a micrograph of the specimen. On their way through the specimen the electrons can be transmitted directly (unscattered) or become scattered, where electron scattering can be influenced by sample thickness, elemental composition and Bragg diffraction¹¹. In bright field imaging the scattered electrons are blocked and the main contribution to the image stems instead from the unscattered ones. In that way, image contrast is obtained by a weakened intensity of electrons in areas where they are scattered. At the same time as an image is formed, so is also the corresponding diffraction pattern (located in the back focal plane) that can be viewed by allowing it to be projected onto the viewing screen or camera. The diffraction pattern contains a representation of the reciprocal lattice and thus allows for complementary crystal structure determination. By inserting an aperture into the beam it is also possible to select a small region of the real space image and form a selected area diffraction pattern. This technique is used together with bright field imaging in Paper 4 to study crystal structure and microstructure in biaxially textured Cr films.

In order to acquire TEM micrographs, very thin samples (≤ 100 nm) are needed for the analysis, and typically thinner is better. This puts high demands on sample preparation. In this thesis, all samples are prepared by cutting out two small pieces ($\sim 0.8 \times 1.8$ mm) that are mounted in a Ti grid with film sides facing each other. This assembly is then mechanically polished down to ~ 50 μm before being Ar ion milled to electron transparency.

5.5.3 Scanning transmission electron microscopy

A scanning transmission electron microscope (STEM) is a type of TEM that unlike the one described in the previous section (Sec. 5.5.2) focuses an electron beam to a small spot that is raster scanned across a specimen. The intensity of transmitted electrons is then detected. By using a high angle annular dark field (HAADF) detector during STEM operation it is possible to obtain mass contrast in the micrographs. This is achieved by detecting electrons scattered at higher angles than what is typical for Bragg diffraction in order to remove its contribution from image formation. Therefore, image contrast is primarily affected by atomic mass and specimen thickness. The mass contrast arises since heavier elements scatter more electrons as compared to lighter ones, and the intensity has been shown to be proportional to the atomic number Z as $Z^{1.7}$ [155]. As mentioned, specimen thickness also affects intensity contrast [156], but assuming that the thickness is constant in a small enough region it is possible to obtain Z contrast in the micrographs with heavier elements appearing brighter. The HAADF STEM characterization technique is employed in Papers 5 and 6 to study the effect of compositional modulation in Ag-Cu and Ag-Au films induced by the MIMSI deposition technique (see Sec. 3.4).

¹¹ The concept of Bragg diffraction is presented later in Sec. 5.7.

5.5.4 Energy dispersive X-ray spectroscopy

On top of acquiring micrographs when irradiating a specimen with electrons, it is also possible to identify the chemical elements within the specimen using energy dispersive X-ray spectroscopy (EDS). This is achieved by detecting elemental specific X-rays emitted from electronic relaxations that occur as an electron from one of the inner shells is knocked out by an irradiating electron. When combined with STEM, it is possible to achieve elemental mapping. Such EDS maps are acquired in Paper 6 to determine the compositional modulation in Ag-Au films induced by the MIMSI deposition technique (see Sec. 3.4).

5.6 Atomic force microscopy

Atomic force microscopy (AFM) is a type of scanning probe microscopy used in various types of fields to study surfaces. Today, it is routinely used to gain topographical information of surfaces.

The AFM employs a cantilever with a very sharp tip that is brought close to a specimen's surface, where the force acting on the tip causes the cantilever to deflect. This deflection is then measured using a laser (see Fig. 5.7). If the tip is positioned at atomic distances from the surface, the cantilever experiences a repulsive force and the AFM is said to operate in contact mode. By raster scanning the surface at a constant cantilever force, achieved by adjusting the tip vertically via feedback from the laser, a topographical map of the surface is acquired. A downside with contact mode is that the surface might be damaged as the tip is dragged across. Therefore, a non-contact mode has been developed, where the cantilever instead oscillates at or near its resonance frequency above the surface. This causes the tip to experience attractive forces

Fig. 5.7. Schematic illustration of the basic principles of atomic force microscopy (AFM) where a sharp tip attached to a cantilever is scanned across a surface to create a topographical image.

from the surface that decreases the oscillations. A topographical image can then be created in the same manner as in contact mode, but by instead keeping the oscillation frequency or amplitude constant. This makes it possible to image soft surfaces (e.g., organic specimens) without any induced damage. However, if used at ambient conditions, where e.g., water easily condenses on the surface, non-contact mode AFM yields the topography of the contaminant instead of the surface. These problems are circumvented by using a combination of the two operation modes where the tip is alternately brought into contact with the surface and then lifted up from the surface to avoid damage creation. This is referred to as tapping mode and is the operation mode utilized in Paper 2 to study the morphology of thin Ag films.

5.7 X-ray diffractometry

X-ray diffraction (XRD) is a non-destructive characterization technique that relies on diffraction from a periodic structure and is used to gain insight to the crystal structure of a specimen. It is based on Bragg's law (illustrated in Fig. 5.8), which gives the condition for constructive interference of X-rays diffracted by a set of crystal planes as

$$2d_{hkl} \sin \theta = j\lambda. \quad (5.7.1)$$

Here, d_{hkl} is the spacing between the (hkl) lattice planes, θ the incidence angle of the X-rays as measured from the sample's surface, j an integer and λ the wavelength of the radiation.

Fig. 5.8. Schematic illustration of constructive interference of X-rays diffracted by a crystal.

5.7.1 θ - 2θ scan

The most common mode of operation in XRD is the θ - 2θ scan in which the movement of the X-ray tube and detector is coupled to always maintain the same incidence angle, θ , of the X-rays as the detection angle. This means that a diffraction pattern is obtained by scanning θ and detecting the diffracted intensity at 2θ . For angles where Eq. (5.7.1) is fulfilled, high intensity Bragg peaks arise. The peak positions can be used to calculate lattice constants and in turn provide e.g., elemental identification, crystal structure determination and stress state. For multilayered specimens, additional satellite peaks can also arise around the main diffraction peak from which the multilayer period can be estimated [157]. The existence of these satellite peaks in multilayered samples is utilized in Paper 5 to determine the transition from multilayer to non-multilayer films as the arrival pattern of the vapor fluxes is varied when using the MIMSI deposition technique (see Sec. 3.4).

5.7.2 Pole figure measurements

The θ - 2θ scan is limited to diffraction of planes that are parallel to the substrate surface, and does thus not provide any information of planes that are oriented differently. This limitation can be overcome by measuring the orientation distribution of specific lattice planes in the sample using pole figure measurements. A pole figure is obtained by specifying θ , corresponding to a specific (hkl) plane (cf. Eq. (5.7.1)), and position X-ray source and detector to allow for diffraction at this angle. The sample is then scanned by successively varying its tilt angle ψ ($0 \leq \psi \leq 90^\circ$) and rotation angle ϕ ($0 \leq \phi \leq 360^\circ$) while keeping θ constant as depicted in Fig. 5.9. This yields an intensity distribution with respect to the specimen from which the orientations (both out-of-plane and in-plane) of the grains in the film can be elucidated. This method is employed in Paper 4 to determine the preferred out-of-plane and in-plane orientations of biaxially aligned Cr films.

Fig. 5.9. Schematic illustration of a pole figure measurement where θ is held constant while ψ and ϕ are varied.

5.8 X-ray reflectometry

X-ray reflectometry (XRR) is a non-destructive analysis technique that is widely used to determine properties, such as thickness and density, of thin films. It is based on reflection from layers with different electron densities within a specimen, and not on diffraction from individual atomic planes as in XRD (see Sec. 5.7).

In XRR, a specimen is irradiated with X-rays at grazing incidence and the reflected intensity is detected at the same angle. As long as the incidence angle is small, as measured from the specimen's surface, total reflection occurs at the surface, but above a critical angle some of the X-rays penetrate into the specimen. These X-rays can, in turn, be reflected or transmitted as they encounter the film-substrate, and later also the film-ambient, interface. By detecting the intensity of outgoing X-rays, an interference pattern containing so called Kiessig fringes is obtained when scanning the incident angle as seen in Fig. 5.10. The fringes are due to the finite thickness of the film, and the separation between them can be used to determine the total film thickness. This is utilized in Papers 1, 5 and 6 to determine deposition rates. Furthermore, in multilayered samples additional interfaces are also present within the film. They give rise to additional interference maxima whose separation is coupled to the multilayer period. The existence of such multilayer peaks are used in Paper 5 to determine the transition from a multilayer to a non-multilayer structure for Ag-Cu films deposited by the MIMSI method (see Sec. 3.4).

Fig. 5.10. Typical X-ray reflectivity (XRR) pattern of a Mo film.

Summary and contributions to the field

My research has focused on the structure forming processes of vapor phase deposited metal thin films grown at far-from-equilibrium conditions. Below are the conclusions I draw from my work and the contribution it may have on the field.

Metal thin film growth on weakly bonding substrates is a well-known example where three dimensional islands nucleate, grow and coalesce on the substrate surface before forming a continuous film. These initial growth stages are thus decisive for the resulting microstructure of the films and can e.g., yield different continuous film formation thicknesses. This is one of the characteristic transition thicknesses that I have studied in Papers 1 and 2 in order to understand the individual and the combined effect of the initial growth stages on film formation and morphology evolution. As model system and representative case of three-dimensional island growth Ag is grown on SiO_2 using pulsed vapor fluxes at different pulsing frequencies. By doing so I demonstrate that nucleation and island growth occur in the same way irrespective of the time in between vapor pulses. The coalescence completion rate is however shown to vary with frequency, where a longer time in between pulses causes more coalescence events to be completed. This is valid up to a certain frequency, above which in principle no coalescence events are completed owing to faster island growth rates. Two different regimes are thus present where coalescence is either active or not. This means that it is possible to tailor the microstructure by allowing or not coalescence to be completed, which e.g., can give rise to bimodal or monomodal island size distributions, respectively. The fact that nucleation and island growth conditions are found to be unaltered irrespective of vapor flux modulation would also make it possible to achieve identical initial conditions for future studies concerning dynamics of coalescence and void filling processes. The knowledge generated can in addition be used as basis to control the morphology of other metallic systems grown on weakly bonding substrates. One such example is metals grown on graphene where the metal potentially could be employed as electrical contacts, or as active material in catalytic and plasmonic applications [11].

Another way to affect the films microstructure is by changing the incidence angle of the vapor flux so that it arrives at a non-zero angle with respect to the substrate surface normal. Films do then typically exhibit a voided columnar structure that tilts towards the vapor source due to shadowing of the vapor flux from adjacent islands/columns. The specific angle at which these columns tilt away from the substrate surface normal and how this angle changes with growth conditions is commonly employed as a way to understand how growth proceeds. This is the angle that I have studied in Paper 3 for Cu and Cr—two materials with distinctly different nucleation behaviour—grown on SiO_2 to understand the effect of the initial growth stages on film formation. Based on the results I suggest that the column tilt angle is set by the nucleation conditions in conjunction with shadowing of the vapor flux from adjacent islands. This previously unexplored correlation could thus (at least partly) be the reason for the commonly observed material specific differences of the column tilt angle and hence give new insight into the physical processes that determine structure formation in these films.

For some materials that are grown from vapor fluxes arriving at an angle, a biaxial alignment that exhibits preferred out-of-plane and in-plane orientations can also develop in the films. In order to describe the origin of the in-plane alignment, an evolutionary growth model based on competition between differently in-plane oriented grains has been suggested [24]. This model does however overlook the fact that all islands do not exhibit the same out-of-plane orientation during the early stages of growth, making it inconsistent with the experimental reality. In order to replicate the model's growth conditions this assumption would thus need to be eliminated. This is done in Paper 4 by using a uniaxial buffer layer that impose a specific out-of-plane orientation while still maintaining a random in-plane orientation. By doing so I show that a double in-plane alignment can develop even though one of the alignments is predicted to be less favored. The existence of a double in-plane alignment has previously been predicted by the model, but it has not been observed in experiments. This suggests that additional processes not included in the current model are decisive for the development of the in-plane alignment in biaxially aligned thin films grown without a uniaxial buffer layer.

Additional film properties can be obtained by alloying different elements with each other. In that case, properties are largely determined by chemistry, i.e., the specific elements and their composition, and by how the different elements are arranged in relation to each other. This atomic arrangement is determined by thermodynamics and kinetics, but can also be altered by high resolution vapor flux modulation. Such fluxes are here accessed via the MIMSI synthesis technique described in Sec. 3.4 and used as a key component in a research methodology that allows for understanding the combined effect of thermodynamics, kinetics and flux modulation on the atomic arrangement. The methodology is presented in Papers 5 and 6 where it is used to study two thermodynamically different model systems, the immiscible Ag-Cu and the miscible Ag-Au systems. The results reveal that structure formation is determined by Ag atoms capping newly deposited Cu atoms and by a rough morphology

of the Ag-Au growth front for each respective system. The presented methodology can thus be used to identify and understand structure forming process in multicomponent materials and in that way be used to tailor atomic arrangement and interface atomic structure, and hence tune related properties thereof.

APPENDIX A

Column tilt angle calculations

In this appendix the relations used to calculate the resulting column tilt angles during growth at non-normal incidence angles as presented in Sec. 2.2.6.1 are derived. The resulting equations are based on a hemispherical growth model with all parameters defined in Fig. A.1.

Fig. A.1. Illustration of the geometrical model used to predict the column tilt angle depending on the island radius R and island-island separation L .

In order to find the column tilt angle β , it needs to be related to the vapor flux incidence angle α , the island radius R and the island-island separation L , such that $\beta = \beta(\alpha, R, L)$. The first step in doing so is to establish $\beta = \beta(\alpha, \zeta)$, where ζ is defined in Fig. A.1, and after that find $\zeta = \zeta(\alpha, R, L)$. For ease of computation β is here defined in the same way as in Ref. 79, where the middle of the non-shadowed region is assumed to be the fastest growth direction and thus also the reference point for determination of β . This means that $\beta(\alpha, \zeta)$ can be obtained by finding w as

$$w = \int_{-(\frac{\pi}{2}-\alpha)}^{\zeta} R \cos(\zeta' - \alpha) d\zeta' = R(\sin(\zeta - \alpha) + 1) \quad (\text{A.1a})$$

$$\frac{w}{2} = \int_{\beta}^{\zeta} R \cos(\zeta' - \alpha) d\zeta' = R(\sin(\zeta - \alpha) - \sin(\beta - \alpha)) \quad (\text{A.1b})$$

and equate. The following expression is then obtained

$$2 \sin(\beta - \alpha) = \sin(\zeta - \alpha) - 1, \quad (\text{A.2})$$

which also can be written as

$$\beta = \alpha + \arcsin\left(\frac{\sin(\zeta - \alpha) - 1}{2}\right). \quad (\text{A.3})$$

With Eq. (A.3), $\beta = \beta(\alpha, \zeta)$ is established and it is now time to determine $\zeta = \zeta(\alpha, R, L)$. This is done by first finding the absolute distances from the island centre to P_1 and P_2 in the x - and y -directions

$$x_1 = R \cos \alpha \quad (\text{A.4a})$$

$$y_1 = R \sin \alpha \quad (\text{A.4b})$$

$$x_2 = R \sin \zeta \quad (\text{A.4c})$$

$$y_2 = R \cos \zeta. \quad (\text{A.4d})$$

The above expressions can then be employed in the following relationship for α

$$\tan \alpha = \frac{L - x_1 - x_2}{y_1 - y_2}, \quad (\text{A.5})$$

which when inserted and rearranged gives

$$\cos \alpha + \tan \alpha \sin \alpha - \frac{L}{R} + \sin \zeta = \tan \alpha \cos \zeta. \quad (\text{A.6})$$

By introducing the two constants

$$C_1 = \cos \alpha + \tan \alpha \sin \alpha - \frac{L}{R} \quad (\text{A.7a})$$

$$C_2 = \tan \alpha \quad (\text{A.7b})$$

and squaring both sides Eq. (A.6) can be written as

$$(C_1 + \sin \zeta)^2 = C_2^2 \cos^2 \zeta. \quad (\text{A.8})$$

In turn, this expression can be rewritten, using the Pythagorean trigonometric identity and completing the square, as

$$\zeta = \arcsin\left(\frac{-C_1 \pm (C_2^2 + 1 - C_1^2)^{\frac{1}{2}}}{1 + C_2^2}\right). \quad (\text{A.9})$$

Combining Eqs. (A.3) and (A.9) finally yields an expression of the form

$$\beta = \beta(\alpha, L/R). \tag{A.10}$$

The results are presented in Sec. 2.2.6.1.

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- I. Time-domain and energetic bombardment effects on the nucleation and coalescence of thin metal films on amorphous substrates**
D. Magnfält, V. Elofsson, G. Abadias, U. Helmersson and K. Sarakinos.
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- II. Unravelling the physical mechanisms that determine microstructural evolution of ultrathin Volmer-Weber films**
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- V. Atomic arrangement in immiscible Ag-Cu alloys synthesized far-from-equilibrium**
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Acta Mater. **110** (2016) 114.
- VI. Structure forming processes in miscible and immiscible compounds grown far-from-equilibrium**
V. Elofsson, G. A. Almyras, B. Lü, M. Garbrecht, R. D. Boyd and K. Sarakinos.
In manuscript.

My contribution to the papers

- I. I was involved in planning the experiments, performed part of the film synthesis and all film characterization and analysis by spectroscopic ellipsometry. I also took part in writing the paper.
- II. I was responsible for planning large part of the experiments, performed major part of the film synthesis and all film characterization and analysis by spectroscopic ellipsometry. I also wrote major part of the paper.
- III. I was responsible for the planning and performed all depositions, characterization and analysis. I also wrote major part of the paper.
- IV. I was responsible for the study and performed all depositions, characterization (except for the TEM imaging) and analysis. I wrote the paper.
- V. I was responsible for planning large part of the study and performed all depositions as well as the XRD/XRR characterization and analysis. I also took part in writing the paper.
- VI. I was responsible for planning large part of the study and performed the depositions and part of the analysis. I wrote the paper.

- VII. Experimental validation of nanoscale aggregation theory in non-wetting systems**
B. Lü, L. Souqui, V. Elofsson and K. Sarakinos.
Submitted for publication.
- VIII. Theoretical and experimental study of metastable solid solutions and phase stability within the immiscible Ag-Mo binary system**
K. Sarakinos, G. Greczynski, V. Elofsson, D. Magnfält, H. Högberg and B. Alling.
J. Appl. Phys. **119** (2016) 095303.
- IX. Dynamic competition between island growth and coalescence in metal-on-insulator deposition**
B. Lü, V. Elofsson, E. P. Münger and K. Sarakinos.
Appl. Phys. Lett. **105** (2014) 163107.
- X. Atomistic view on thin film nucleation and growth by using highly ionized and pulsed vapour fluxes**
K. Sarakinos, D. Magnfält, V. Elofsson and B. Lü.
Surf. Coat. Technol. **257** (2014) 326.

Appended papers

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