Linköping Studies in Science and Technology
Dissertation No. 2084

Thin metal films on weakly-interacting substrates

Nanoscale growth dynamics, stress generation,
and morphology manipulation

Andreas Jamnig

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Cover image:

Lines: Evolution of stress-film thickness product with time during and post-deposition of thin silver films on weakly-interacting silicon oxide

Left: Coalescing silver islands, imaged by scanning electron microscopy

Top: Surface topography of a silver film, imaged by atomic force microscopy

Bottom: Microstructure of a silver film, imaged by cross-sectional transmission electron microscopy

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Thin metal films on weakly-interacting substrates

Nanoscale growth dynamics, stress generation,
and morphology manipulation

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Abstract

Vapor-based growth of thin metal films with controlled morphology on weakly-interacting substrates (WIS), including oxides and van der Waals materials, is essential for the fabrication of multifunctional metal contacts in a wide array of optoelectronic devices. Achieving this entails a great challenge, since weak film/substrate interactions yield a pronounced and uncontrolled 3D morphology. Moreover, the far-from-equilibrium nature of vapor-based film growth often leads to generation of mechanical stress, which may further compromise device reliability and functionality. The objectives of this thesis are related to metal film growth on WIS and seek to: (i) contribute to the understanding of atomic-scale processes that control film morphological evolution; (ii) elucidate the dynamic competition between nanoscale processes that govern film stress generation and evolution; and (iii) develop methodologies for manipulating and controlling nanoscale film morphology between 2D and 3D. Investigations focus on magnetron sputter-deposited Ag and Cu films on SiO₂ and amorphous carbon (a-C) substrates. Research is conducted by strategically combining of *in situ* and real-time film growth monitoring, *ex situ* chemical and (micro)-structural analysis, optical modelling, and deterministic growth simulations.

In the first part, the scaling behavior of characteristic morphological transition thicknesses (i.e., percolation and continuous film formation thickness) during growth of Ag and Cu films on a-C are established as function of deposition rate and temperature. These data are interpreted using a theoretical framework based on the droplet growth theory and the kinetic freezing model for island coalescence, from which the diffusion rates of film forming species during Ag and Cu growth are estimated. By combining experimental data with *ab initio* molecular dynamics simulations, diffusion of multiatomic clusters, rather than monomers, is identified as the rate-limiting structure-forming process.

In the second part, the effect of minority metallic or gaseous species (Cu, N₂, O₂) on Ag film morphological evolution on SiO₂ is studied. By employing *in situ* spectroscopic ellipsometry, it is found that addition of minority species at the film growth front promotes 2D morphology, but also yields an increased continuous-layer resistivity. *Ex situ* analyses show that 2D morphology is favored because minority species hinder the rate of coalescence completion. Hence, a novel growth manipulation strategy is compiled in which minority species are deployed with high temporal precision to selectively target specific film growth stages and achieve 2D morphology, while retaining opto-electronic properties of pure Ag films.

In the third part, the evolution of stress during Ag and Cu film growth on a-C and its dependence on growth kinetics (as determined by deposition rate, substrate temperature) is systematically investigated. A general trend toward smaller compressive stress magnitudes with increasing temperature/deposition rate is found, related to increasing grain size/decreasing adatom diffusion length. Exception to this trend is found for Cu films, in which oxygen incorporation from the residual growth atmosphere at low deposition rates inhibits adatom diffusivity and

decreases the magnitude of compressive stress. The effect of N_2 on stress type and magnitude in Ag films is also studied. While Ag grown in N_2 -free atmosphere exhibits a typical compressive-tensile-compressive stress evolution as function of thickness, addition of a few percent of N_2 yields to a stress turnaround from compressive to tensile stress after film continuity which is attributed to giant grain growth and film roughening.

The overall results of the thesis provide the foundation to: (i) determine diffusion rates over a wide range of WIS film/substrates systems; (ii) design non-invasive strategies for multifunctional contacts in optoelectronic devices; (iii) complete important missing pieces in the fundamental understanding of stress, which can be used to expand theoretical descriptions for predicting and tuning stress magnitude.

Résumé

La morphologie de films minces métalliques polycristallins élaborés par condensation d'une phase vapeur sur des substrats à faible interaction (SFI) possède un caractère 3D intrinsèque. De plus, la nature hors équilibre de la croissance du film depuis une phase vapeur conduit souvent à la génération de contraintes mécaniques, ce qui peut compromettre davantage la fiabilité et la fonctionnalité des dispositifs optoélectroniques. Les objectifs de cette thèse sont liés à la croissance de films métalliques sur SFI et visent à : (i) contribuer à une meilleure compréhension des processus à l'échelle atomique qui contrôlent l'évolution morphologique des films ; (ii) élucider les processus dynamiques qui régissent la génération et l'évolution des contraintes en cours de croissance ; et (iii) développer des méthodologies pour manipuler et contrôler la morphologie des films à l'échelle nanométrique. L'originalité de l'approche mise en œuvre consiste à suivre la croissance des films *in situ* et en temps réel par couplage de plusieurs diagnostics, complété par des analyses microstructurales *ex situ*. Les grandeurs mesurées sont confrontées à des modèles optiques et des simulations atomistiques.

La première partie est consacrée à une étude de comportement d'échelonnement des épaisseurs de transition morphologiques caractéristiques, à savoir la percolation et la continuité du film, lors de la croissance de films polycristallins d'Ag et de Cu sur carbone amorphe. Ces grandeurs sont examinées de façon systématique en fonction de la vitesse de dépôt et de la température du substrat, et interprétées dans le cadre de la théorie de la croissance de gouttelettes suivant un modèle cinétique décrivant la coalescence d'îlots, à partir duquel les coefficients de diffusion des espèces métalliques sont estimés. En confrontant les données expérimentales à des simulations par dynamique moléculaire *ab initio*, la diffusion de clusters multiatomiques est identifiée comme l'étape limitante le processus de croissance.

Dans la seconde partie, l'incorporation, et l'impact sur la morphologie, d'espèces métalliques ou gazeuses minoritaires (Cu, N₂, O₂) lors de la croissance de film Ag sur SiO₂ est étudié. A partir de mesures ellipsométriques *in situ*, on constate que l'addition d'espèces minoritaires favorise une morphologie 2D, entravant le taux d'achèvement de la coalescence, mais donne également une résistivité accrue de la couche continue. Par conséquent, une stratégie de manipulation de la croissance est proposée dans laquelle des espèces minoritaires sont déployées avec une grande précision temporelle pour cibler sélectivement des stades de croissance de film spécifiques et obtenir une morphologie 2D, tout en conservant les propriétés optoélectroniques des films d'Ag pur.

Dans la troisième partie, l'évolution des contraintes résiduelles lors de la croissance des films d'Ag et de Cu sur carbone amorphe et leur dépendance à la cinétique de croissance est systématiquement étudiée. On observe une tendance générale vers des amplitudes de contrainte de compression plus faibles avec une augmentation de la température/vitesse de dépôt, liée à l'augmentation de la taille des grains/à la

diminution de la longueur de diffusion des adatoms. Également, l'ajout dans le plasma de N_2 sur le type et l'amplitude des contraintes dans les films d'Ag est étudié. L'ajout de quelques pourcents de N_2 en phase gaz donne lieu à un renversement de la contrainte de compression et une évolution en tension au-delà de la continuité du film. Cet effet est attribué à une croissance anormale des grains géants et le développement de rugosité de surface.

L'ensemble des résultats obtenus dans cette thèse fournissent les bases pour : (i) déterminer les coefficients de diffusion sur une large gamme de systèmes films/SFI; (ii) concevoir des stratégies non invasives pour les contacts multifonctionnels dans les dispositifs optoélectroniques; (iii) apporter des éléments de compréhension à l'origine du développement de contrainte, qui permettent de prédire et contrôler le niveau de contrainte intrinsèque à la croissance de films minces polycristallins.

Populärvetenskaplig sammanfattning

Varje material är i ett ständigt samspel med sin omgivning och interaktionens natur bestäms till stor del av materialets yta. Genom att belägga material med en tunn film av ett annat ämne kan man påverka detta samspel, och på så sätt uppnå t.ex. nya optiska och elektriska egenskaper. Denna metod har visat sig ha flertalet nya tillämpningar, bland annat vid skapandet av elektroniska komponenter, solceller och energibesparande fönster. Som namnet antyder är tjockleken på tunna filmer försvinnande liten, och sträcker sig från några atomer till några mikrometer (1 mikrometer = 0,001 millimeter). Tunnfilm syntetiseras vanligtvis genom så kallade förångningstekniker, där en fast materialkälla omvandlas till ånga och atom för atom skapar en film på ytan (som kallas substrat). Denna process är dock svår att i detalj observera, och på grund av detta analyseras ofta filmbildningen indirekt via tekniker som mäter förändringar av filmens optiska, elektriska och mekaniska egenskaper i realtid.

Denna avhandling undersöker syntesen av och egenskaperna hos myntmetallfilmer, (silver och koppar), på kiseldioxid- och grafitytor. Dock uppvisar dessa ytor endast mycket svaga kemiska bindningar med myntmetallatomerna, vilket medför att metallfilmerna tenderar att skapa en 3D nanostruktur, dvs att metallatomerna hopar sig i isolerade öar. Denna tendens påverkar filmens optiska och elektriska egenskaper negativt och därför begränsas drastiskt möjligheterna att använda metallfilmer i flertalet tillämpningar. Därför fokuserar en del av avhandlingen på att förstå och kontrollera de atomistiska mekanismer som leder till 3D nanostrukturbildning. En annan problematisk aspekt av tunnfilmsyntesen är uppbyggnaden av mekaniska spänningar, som kan leda till böjning av substrat, skapande av sprickor, och att filmen förstörs. Till följd av detta handlar andra delen av avhandlingen om sambandet mellan syntesparametrar och typ/storlek av mekaniska spänningar. Sammanfattningsvis: en bättre förståelse av de atomistiska processerna som styr filmbildning och uppbyggnaden av mekaniska spänningar samt strategier för deras manipulation möjliggör en mer riktad användning av metallfilmer i viktiga tekniska tillämpningar.

Preface

The present dissertation is the result of my doctoral studies carried out between 2016 and 2020 in the Physics and Properties of Nanostructures (PPNa) group at the Institut Pprime, University of Poitiers, France, and the Nanoscale Engineering Division (NADES) at the Department of Physics, Chemistry, and Biology, Linköping University, Sweden.

The first part provides an overview of the research field, and the employed research methods. In the second part, the results of the research performed in course of the doctoral studies are presented in form of appended papers.

My research has been financed by the French Government program “Investissements d’Avenir” (LABEX INTERACTIFS, reference ANR-11-LABX-0017-01) and the ÅForsk foundation (contract ÅF 19-137). I acknowledge travel support by the ÖMSE program of the French Institute of Sweden, and financing of inter-disciplinary collaboration within Linköping University by the Center of Nano Science and Technology.

Andreas Jamnig

Linköping, August 2020

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A Ph.D. student spends many hours at the university. Luckily for me, this is also the place where I met friends, so that coffee, lunch and fika breaks shortened the days, and afterwork prolonged them. Senda, you were the first person to welcome me into the Ph.D. student life and showed me that sometimes it is better not to take things too seriously, thank you for that. Our hikes with Damien and Julien were amazing, and evenings with Florian, Romain, Romuald were always fun. Benjamin and Maxime, thank you becoming good friends.

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1. Introduction

Thin metal films are critical components in many technologies that have become essential parts of modern life, including information storage systems, integrated circuits, sensors, and displays. [1] This is a direct result of the electronic, optical, magnetic, mechanical, and thermal properties that are unique to metallic materials. These properties are largely established during film synthesis, [2–4] and can often not be changed post-synthesis without losing unique film attributes. Thus, a fundamental understanding of nanoscale structure-forming processes that govern film growth is needed to effectively control performance and functionality of thin-film-based devices.

Noble-metal atoms interact weakly with the surface of oxides and van der Waals materials. [5,6] This weak interaction leads to a pronounced and uncontrolled three-dimensional (3D) film morphological evolution, which is characterized by discontinuous layers during the initial film growth stages, and rough surfaces upon formation of a continuous layer. [7] A 3D morphology is detrimental for applications that require flat film surfaces, e.g., in optoelectronic devices, biosensors, and low-emissivity energy-saving windows. [8–11] Since 3D growth is an intrinsic property of weakly-interacting film/substrate systems, special deposition strategies are required for manipulating growth toward two-dimensional (2D) morphology. While such strategies exist in the literature for epitaxial systems, e.g., via deployment of minority species (also referred to as surfactants) at the film growth front, [12] the way by which structure-forming processes in weakly-interacting systems are affected by the presence of surfactant atoms is not fully understood.

Vapor-based thin-film deposition is a far-from-equilibrium process, whereby structure formation is determined by the kinetic rates of atomic-scale mechanisms. [12] At such conditions, atoms often arrange themselves in metastable configurations, leading to the formation of mechanical stress, [13] which can be detrimental for the reliability and functionality of thin-film-based devices. Stress formation and evolution is strongly linked to the film morphology at various growth stages, during which a multitude of processes, including surface diffusion and grain growth, are active. [14,15] To date, it remains unclear how the complex interplay and the dynamic competition among these processes affect stress.

Research presented in this thesis focuses on the nanoscale growth dynamics, stress generation, and morphology manipulation in weakly-interacting film/substrate systems. Investigated films consist of silver and copper; a short introduction to the properties of these elements is given in Section 1.1. The research goal and strategy are presented in Section 1.2, and an outline of the thesis is given in Section 1.3.

1.1. Silver and copper

Silver and copper are members of group 11 in the periodic table of elements, and together with gold, are known as coinage metals. An overview of physical and chemical properties of silver and copper is given in Table 1. [16]

Silver has been known since ancient times because it exists in elemental form on earth's surface. Silver-based compounds that can be found naturally include sulfides and chlorides. Pure silver is stable in pure water and air, and has a brilliant white metallic luster that tarnishes when exposed to ozone, hydrogen sulfide, or air containing sulfur. It is used as mirror material, when deposited on glass or metals, since it is the best reflector in the visible-light spectral range, but it is a poor reflector in ultra-violet. Silver is ductile and malleable, and has the highest electrical and thermal conductivity of all elements, which is why it is used as ohmic contact material in microelectronics. Pure silver is not toxic, however, many of its salts are, and it is germicidal, i.e., lower organisms do not survive on silver surfaces.

Copper has been known since prehistoric times because it exists on the earth's surface with high purity. Naturally found compounds are oxides, sulfides, and carbonates. Pure copper has a reddish color and a metallic luster. Since pure copper is malleable and ductile, it is one of the first metallic materials that was used as tool by mankind (together with tin and lead). The recognition that a mixture of copper and tin, i.e., bronze, leads to a harder and stronger material than its constituents marks the invention of alloying, and the beginning of a new civilizational age—the bronze age. Copper is the best conductor of heat and electricity after silver, and therefore widely used in the electrical industry.

Thin silver and copper films in oxide/metal/oxide or dielectric/metal/dielectric heterostructures are used as low-emissivity coatings, e.g., on window glass. [11] Owing to the high corrosion resistance and flexibility, these structures are prime candidates to replace indium tin oxide as transparent conductive electrode material in optoelectronic devices including light-emitting diodes, thin-film solar cells, flat-panel displays, and touchscreens. [17] Silver is used in analytical sensors due to the plasmonic behavior of nanoscale silver films and particles, leading to surface enhanced Raman scattering (SERS), which increases sensitivity of biosensors. [18]

Table 1: Overview of physical and chemical properties of Cu and Ag as listed in Ref. [1].

	Cu	Ag
Atomic number	29	47
Electronic configuration	$[Ar]3d^{10}4s^1$	$[Kr]4d^{10}5s^1$
Molecular weight (g/mol)	63.546	107.868
Mass density (g/cm^3)	8.96	10.5
Crystal structure	Face centered cubic	
Lattice parameter (nm)	0.36150	0.40862
Melting temperature (K)	1358	1235
Homologous temperature at 300 K	0.22	0.24
Boiling temperature (K)	2835	2435
Gibbs energy of formation of gas at 298.15 K (kJ/mol)	297.7	246.0
Bond dissociation energy (BDE) (kJ/mol)	201	162.9 ± 2.9
BDE with oxygen (kJ/mol)	287.4 ± 11.6	221 ± 21
BDE with sulfur (kJ/mol)	274.5 ± 14.6	216.7 ± 14.6
Electronegativity	1.90	1.93
Electrical resistivity at 298.15 K ($\mu\Omega cm$)	1.543	1.467
Molar heat capacity ($J/(molK)$)	24.440	25.350
Thermal conductivity at 300 K ($W/(cmK)$)	4.01	4.29

1.2. Research goal and strategy

The overall goal of the present thesis is to contribute to the understanding of fundamental aspects related to morphological evolution and stress generation during noble-metal film growth on weakly-interacting substrates. The specific objectives are to:

- Elucidate atomic-scale processes that control early film growth stages, and estimate the rates of such processes.
- Understand the way by which key deposition parameters (e.g., deposition rate and temperature) affect stress evolution, and establish the complex interplay among stress and film microstructure and morphology.
- Obtain atomistic insights with regards to the effect of gaseous and metallic surfactants on early stages of film growth, and leverage these insights for developing efficient non-invasive growth manipulation strategies.

Investigations focus on magnetron sputter-deposited silver and copper films on silicon dioxide and amorphous carbon substrates, which are archetypal weakly-interacting film/substrate systems. Research is conducted by strategically combining *in situ* and real-time film growth monitoring by means of multiple complementary diagnostic tools, *ex situ* chemical and (micro)-structural analyses, optical modelling, and deterministic growth simulations.

1.3. Outline of the thesis

This thesis work is divided into two parts. The first part (Chapters 1 through 7), is a topical, theoretical, and experimental introduction to the research performed throughout my Ph.D. studies. Concepts related to vapor-based thin film synthesis (i.e., vacuum science and technology, plasma physics, sputter-deposition) are described in Chapter 2. An overview of atomic-scale structure-forming processes during film growth is given in Chapter 3. Concepts that explain stress formation and evolution in thin films are presented in Chapter 4. Chapter 5 describes experimental devices and techniques that are employed in course of this thesis work, and Chapter 6 outlines employed simulation and theoretical techniques. Chapter 7 outlines contributions to the research field and provides an outlook for a potential continuation of the research conducted in the present work. In the second part, papers that present my main contributions to the research field are appended.

2. Vapor-based thin film deposition

Vapor-phase condensation is the most common method for synthesizing thin films for research and industrial purposes. In the present thesis, thin films are synthesized by magnetron sputtering, a deposition method in which vapor is generated by transferring momentum from energetic ions to a solid source. To be able to control the film synthesis environment, deposition experiments are routinely carried out in vacuum, hence a brief introduction to vacuum science and technology is provided in Section 2.1. The source of energetic ions required in sputter-deposition is a plasma; this state of matter is introduced in Section 2.2. Finally, the principle of magnetron sputter-deposition is presented in Section 2.3.

2.1. Vacuum science and technology

Vacuum is per definition space void of matter. To create vacuum from the atmosphere, gas molecules have to be removed from a closed isolated vessel (referred to as vacuum chamber). However, the complete removal of atoms is technologically not possible, such that in materials science the term “vacuum” refers to a volume with pressure lower than atmospheric pressure, [19] i.e., vacuum in thin film deposition chambers is a gas. Consequently, atom/molecule interactions with each other and with surfaces are described by the kinetic theory of gases. This theory predicts the speed distribution of gas atoms, from which the frequency of collisions in the gas phase and the flux of gas species toward the solid surface can be calculated (Section 2.1.1). These quantities are important for determining the energy and chemical nature of film forming species, as well as the incorporation of impurities in the film as explained in Section 2.1.2. Key technological aspects of vacuum science, i.e., principles and types of vacuum pumps and pressure gauges are outlined in Sections 2.1.3 and 2.1.4, respectively.

2.1.1. *Kinetics of atoms in gas phase*

The kinetic theory of gases describes the behavior of ideal gases in a confined volume, assuming random motion of gas molecules that are approximated as hard spheres with dimensions that are small compared to the mean molecule distance. Molecule-molecule and molecule-wall interactions are treated as elastic collisions, while no attractive or repulsive forces apply between gas molecules. With these approximations, the Maxwell-Boltzmann formula describes the steady-state distribution of molecular speeds v as [20,21]

$$f(v) = \frac{1}{n} \frac{dn}{dv} = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 \exp \left(-\frac{mv^2}{2k_B T} \right). \quad (2.1)$$

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In Eq. 2.1, $f(v)$ is the fractional number of molecules, n is the number of molecules per unit volume in the speed range v to $v + dv$, m is the molecular mass, k_B is the Boltzmann constant, and T is the absolute temperature. From this distribution function, we find that no molecules with zero or infinite speed exist. The root-mean-square speed $\sqrt{\overline{v^2}}$, which describes the collective behavior of the gas molecules, calculates as $\sqrt{\overline{v^2}} = \sqrt{3k_B T/m}$.

Speed distributions for He and Ar gas are presented in Fig. 2.1, and we find that $f(v)$ broadens and shifts toward larger speed values with decreasing m (e.g., $m_{He} = 4 u$, and $m_{Ar} = 40 u$), which is also reflected by the relation $\overline{v^2} \sim 1/m$ (indicated by vertical lines in Fig. 2.1). When comparing $f(v)$ of Ar at 300 and 1000 K, a shift of the distribution to larger speed and broadening is seen for increasing T ; concurrently, $\overline{v^2}$ scales linearly with T . It is noted that while the speed distribution is dependent on m and T , the kinetic energy E_{kin} of a collection of gas molecules calculates as [20,21]

$$E_{kin} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T, \quad (2.2)$$

and is only temperature dependent.

Fig. 2.1: Speed distributions of Ar and He gas calculated by the Maxwell-Boltzmann formalism for temperatures 300 K (Ar and He), and 1000 K (Ar). The root-mean-square speeds of the respective distributions are marked by vertical lines.

2.1.2. Gas/gas and gas/surface interactions

As explained in Section 2.1.1, molecules in a contained volume interact with the walls that limit the volume, and apply a pressure $p = nm\overline{v^2}/3 = nk_B T$. [20,21] Vacuum systems are categorized by the lowest pressure they can reach, i.e., the base pressure. Low/intermediate-vacuum systems have base pressure between atmosphere ($10^5 Pa$) and $10^{-1} Pa$, high-vacuum (HV) systems are in the range 10^{-1}

2.1 Vacuum science and technology

to 10^{-5} Pa , while ultra-high-vacuum (UHV) is reached for $p < 10^{-5} \text{ Pa}$. Ambient atmosphere consists mainly of nitrogen molecules, however, an artificially created HV contains predominantly water vapor, and hydrogen molecules are the most abundant species in UHV. This is a result of gas-dependent pumping rates in artificial vacuum systems.

From the Maxwell-Boltzmann speed distribution, the mean free path λ , i.e., the mean distance a gas molecule travels between collisions with other molecules, can be calculated as [20,21]

$$\lambda = \frac{k_B T}{\sqrt{2} \pi d_{mol}^2 p} . \quad (2.3)$$

In Eq. 2.3, d_{mol} is the diameter of the gas molecule; a typical value of d_{mol} for gases used in thin film deposition is $3 \times 10^{-10} \text{ m}$. [20] At 300 K , λ is in the range 10^{-1} to 10^3 m in HV systems, and consequently comparable to typical vacuum chamber dimensions, i.e., gas molecules experience few/no collisions. However, during deposition of thin films, the working pressure is $\sim 1 \text{ Pa}$, and λ decreases to values $< 10^{-2} \text{ m}$, and gas molecules collide often before they are pumped out of the chamber, or adsorb on a surface.

Another important quantity that can be derived from the Maxwell-Boltzmann speed distribution is the gas impingement flux Φ per unit time and area [20,21]

$$\Phi = n \sqrt{\frac{k_B T}{2\pi m}} = \frac{p}{\sqrt{2\pi m k_B T}} . \quad (2.4)$$

Equation 2.4 can be used to calculate the monolayer formation time t_{ML} of gas species on a surface. During film growth, background species arriving from the gas phase lead to contamination in the film, i.e., deposition of clean films is not possible if the arrival rates of film atoms and gas species from the background are comparable. From d_{mol} , the average area of a gas molecule can be estimated as $d_{mol}^2 \cong 10^{-19} \text{ m}^2$, i.e., one monolayer of gas molecules consists of $\sim 10^{19} \text{ molecules/m}^2$. For thin film growth in a system with base pressure $p = 10^{-5} \text{ Pa}$, where water is the most abundant gas species ($m_{water} = 18 \text{ u}$), one monolayer (ML) forms in $\sim 30 \text{ s}$ at $T = 300 \text{ K}$. Comparing this time to t_{ML} of the film forming species, e.g., during deposition of Cu with deposition rate 0.1 nm/s , $t_{ML,Cu} \cong 2 \text{ s}$, a Cu/H₂O monolayer formation time ratio of $t_{ML,Cu}/t_{ML,water} \cong 0.07$ is calculated, i.e., a Cu film deposited at above-described conditions may contain up to $7 \text{ at. \%}$ of water. This value represents an upper theoretical limit since a sticking probability of 1 for gas molecules on the surface is assumed. In reality, the sticking probability of gases on surfaces is smaller than unity, so that a significantly smaller fraction of contaminants is incorporated in the growing films at typical vacuum conditions.

2.1.3. *Vacuum pumps*

To create sub-atmospheric pressure from the ambient atmosphere, air has to be removed from a closed volume (e.g., deposition chamber). For HV and UHV conditions, this is achieved using a pumping system rather than a single pump, which include a primary pump to create low vacuum down to $\sim 10^{-1} Pa$ that is connected in series to a second pump that is backed by the primary pump and allows reaching HV and UHV. Thin films discussed in this thesis are synthesized in two vacuum systems (HV and UHV). In the following, vacuum pump concepts that are used in the respective deposition chambers are outlined. A more detailed description of the pumping systems is given in Section 5.1.

Positive displacement pumps

Positive displacement pumps are used to create low/rough vacuum with pressure $\sim 10^{-1} Pa$, [20] or to back pumps that can create HV/UHV (see below). Their working principle is the isolation and compression of a volume from the to-be-pumped chamber that is then exhausted into the atmosphere; this volume displacement is usually performed by rotating parts. [22] If lubricant and pumped volume are isolated from each other, the pump is called dry positive displacement pump, which limits the risk of vacuum chamber contamination. [19]

An example of a rotary positive displacement pump is the Roots pump; the working principle is outlined in Fig. 2.2(a). Two lobed rotors spin in an oval housing with opposing directions driven by a motor. [19] When the two rotors are in a horizontal T-configuration, volume is isolated (e.g., right side during (iii) in Fig. 2.2(a)), which is subsequently exhausted in sequence (iv). The rotors touch neither each other nor the housing walls, i.e., no lubrication is needed, but due to the existence of small gaps between rotors and walls ($\sim 0.1 mm$), HV cannot be reached with this pump. High rotation speeds (typically $3000 rpm$) are used to compensate for the incomplete isolation of volume. When pumping against atmospheric pressure, the Roots pump has an ultimate pressure of $\sim 10^3 Pa$, while for attaining backing pressure $\sim 10^{-1} Pa$, several Roots pumps are combined in series.

Another concept is the scroll pump, depicted in Fig. 2.2(b), which consists of two Archimedean spirals that are displaced along a horizontal line, and rotated by 45° . This creates crescent-shaped closed volumes. One spiral is a stator, while the second one rotates, and transports gas from the chamber side toward the exhaust. Tip seals isolate the top of the spiral walls, i.e., no lubrication is needed. The ultimate pressure that can be attained with a scroll pump is $\sim 10^{-1} Pa$.

Fig. 2.2: Operation principle of (a) a Roots pump and (b) a scroll pump. Reprinted with permission from (a) Ref. [22] and (b) Ref. [23].

Cryogenic pumps

Cryogenic pumps trap gas species on surfaces that are cooled to temperatures $< 120\text{ K}$. [20] At such temperatures, van der Waals forces inhibit the desorption of atoms from the surfaces, except for hydrogen, helium and neon that have too high vapor pressures, even at surfaces cooled to 20 K in the innermost section of the pump. A schematic representation of a cryopump is given in Fig. 2.3(a). The pump is shielded from heating by thermal radiation from the surrounding atmosphere, and cryogenic temperatures are obtained by cooling the surfaces with liquid nitrogen. Cryogenic pumps are widely used in materials research due to their high pumping speed, and possibility to reach UHV. They cannot be operated from ambient pressure, since the influx of gas molecules would lead to heating of system, and formation of thick ice condensate, and are therefore coupled with primary pumps that create a pressure $\sim 10^{-1}\text{ Pa}$. To limit the formation of thick condensate, gases are trapped at different stages, with decreasing temperature from the vacuum chamber to the innermost part of the pump.

Turbomolecular pumps

A turbomolecular pump consists of stator/rotor pairs; latter imparts a preferred orientation to the motion of gas molecules by impact, as schematically illustrated in Fig. 2.3(b). [4] While gas molecules are transferred through the pump, they are compressed from low pressures (on the chamber side) to higher pressure (on the backing line side). This compression ratio is proportional to the rotor speed ($> 20\,000\text{ rpm}$), and the inverse of the molecular weight of the pumped species. Therefore, hydrogen is not efficiently captured and removed by this type of pumps. Nonetheless, base pressure in the 10^{-8} Pa -range can be attained with a turbomolecular pump. Moreover, such a pump is not able to compress gases from the UHV regime to ambient pressure and is therefore coupled with a primary pump that creates a foreline pressure $\sim 10^{-1}\text{ Pa}$.

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Fig. 2.3: (a) Schematic representation of a cryogenic pump that contains stages with different temperatures to condensate gas molecules. (b) Schematic representation of a turbomolecular pump. Rotor blades transfer momentum to gas atoms and compress them from the vacuum chamber to the backing line.

2.1.4. Pressure gauges

The discussion in Section 2.1.2 shows that pressure is an important quantity from which the behavior of gas molecules in a vacuum system can be determined, including mean free path and monolayer formation time. Depending on the vacuum type (HV, UHV), different gauges are used to determine the pressure in a vacuum system. In the following, the working principles of some pressure gauges that were used in course of the present thesis are outlined.

Capacitance manometer

Capacitance manometers are classified as direct-reading pressure gauges with a solid wall, and accurately measure pressure in the range 10^5 to 10^{-2} Pa. [21] The gauge consists of two chambers (see Fig. 2.4(a)): a sealed chamber with reference pressure (typically 10^{-5} Pa) and one with the to-be-determined pressure, separated by a diaphragm that acts as capacitor with a fixed counterelectrode. When the pressure changes in the measuring chamber, the deflection of the diaphragm changes, which is read as change in capacitance.

Pirani gauge

The Pirani gauge is an indirect pressure gauge (i.e., pressure is measured by the change in another physical property) that relates the heat transfer between a hot wire (filament) and its surrounding gaseous medium to the pressure. [21] In the low-pressure regime ($\sim 10^2$ to 10^{-2} Pa), heat flow due to free molecules (i.e., conduction) increases linearly with temperature, i.e., the rate of temperature

change can be related to the density of gas molecules. This linear relation is not valid at higher pressures, where convection is active, or at too low pressures, where radiation is the predominant heat-transfer mechanism. In the Pirani gauge, the temperature change is measured by temperature-induced resistivity change in an electrical circuit, i.e., a Wheatstone bridge schematically shown in Fig. 2.4(b). A decrease in electrical resistivity signifies that the wire temperature decreases owing to stronger gas molecule/wire interactions with increasing pressure. Pirani gauges are used in the pressure range 10^1 to 10^{-2} Pa.

Fig. 2.4: (a) Schematic illustration of a capacitance manometer; when the pressure in the vacuum chamber is not equal to the reference pressure, the diaphragm deflects from its zero position, and the capacitance to a stationary electrode changes. (b) Schematic illustration of a Pirani gauge: the filament resistivity changes due to interaction with gases from the vacuum chamber.

The filament is part of a Wheatstone bridge, and its resistivity R_x can be calculated to $R_x = R_2 R_3 / R_4$, when the resistor R_2 is adjusted so that no current flows through the Amperemeter.

Bayard-Alpert gauge

The Bayard-Alpert gauge is a hot filament ionization gauge that relates the current between a collector and a gas that has been ionized by electron impact to the pressure in the gas. [21] Fig. 2.5(a) illustrates this type of pressure gauge. The hot filament acts as electron emitter, while the positive ions are attracted by the collector. This pressure gauge is used in the pressure range 10^{-1} to 10^{-8} Pa; ion/electron recombination limits the application in the high-pressure range, and x-ray photoemission leads to errors in the low-pressure range. Ionization gauges are not true pressure gauges, since the number of positive ions formed through impact ionization is proportional to their number density, but can be used to measure pressure if the temperature remains constant.

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Cold cathode ionization gauge

In cold cathode ionization gauges, electrons are created between a cathode/anode pair, and forced into long spiral trajectories by a magnetic field (see illustration in Fig. 2.5(b)). [21] This increases the gas/electron interaction probability, which increases the ionization current, and eliminates the need of an additional electron source (i.e., the hot filament). Cold cathode ionization gauges are used in the pressure range 10^{-1} to 10^{-9} Pa; the low-pressure limit is reached when no discharge is formed.

Fig. 2.5: (a) Schematic illustration of a hot filament ionization gauge, consisting of the electron (e^-) emitting cathode (i.e., hot filament), anode and collector. Electron/gas molecule interactions can lead to ionization; the ion is attracted by the collector. Impingement of electrons on the anode leads to x-ray emission. (b) Schematic illustration of a cold cathode ionization gauge, where electron density is locally increased by a magnetic field. This increases the interaction probability between electrons and gas molecules travelling from anode to cathode.

2.2. Confined plasma

During sputter-deposition of thin films, a vapor phase is created by bombarding the surface of a solid with ions. The source of these ions is a plasma that is created within the vacuum chamber. This state of matter is introduced in this section, before outlining sputtering and sputter-deposition in Section 2.3.

Most observable mass in the universe is in plasma-state, [4] i.e., it consists of a mixture of positively charged ions, negatively charged electrons, and neutral species, i.e., plasma is, on average, electrically neutral. [24] Plasmas can be categorized in terms of the number density of charged particles (typically $\sim 10^{16} \text{ m}^{-3}$ in laboratory-scale plasmas) and the energy (i.e., temperature) of the species (typically, electron energies range between 1 to 10 eV, ion and neutral energies are in the meV regime). [4] If the plasma is in equilibrium, temperatures of all plasma species are equal to each other and to the temperature of the chamber walls. This condition is never met in the laboratory, i.e., nonequilibrium or *cold plasmas* are used in thin film synthesis experiments.

One important feature is that particles within a plasma move in random directions, but the plasma exhibits a collective behavior in the presence of an electric field, i.e., a particle flux is created which may be used in thin film deposition. Due to random movement within the plasma, particle interactions are common, e.g., electrons and ions (of species A and B) can recombine $e^- + A^+ \rightarrow A$, which leads to loss of charged particles. To maintain a stable plasma, additional processes are needed, e.g., ionization ($e^- + A \rightarrow A^+ + 2e^-$), attachment ($e^- + A \rightarrow A^-$), excitation ($e^- + A_2 \rightarrow A_2^* + e^-$), or dissociative attachment ($e^- + A_2 \rightarrow A^+ + A^- + e^-$). Atom-ion collisions are common, e.g., symmetric charge transfer ($A^+ + A \rightarrow A + A^+$), or metastable-neutral ionization ($A^* + B \rightarrow B^+ + A + e^-$), also known as Penning ionization. [4]

Due to the inequality of electron and ion temperatures in laboratory-scale plasmas, the net-neutrality is not sustained, and plasma interaction with the (electrically conductive) chamber wall leads to the creation of a *sheath* (see Fig. 2.6). Electrons have higher velocities than ions, and are therefore lost faster to the walls, i.e., the plasma has a positive potential with respect to the walls (plasma potential $V_p \cong 5 \text{ V}$). [4,24] Inserting an electrically isolated object into a plasma results initially in a negative charging due to arrival of fast electrons. The negative potential attracts ions, while it repels electrons, until a steady-state electron/ion flux is reached and a negative floating potential $V_f \cong -15 \text{ V}$ of the object is formed with respect to ground. [4,24]

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If a negative potential is applied to the cathode (i.e., the target during sputter-deposition), electrons are accelerated away from the cathode surface, while ions are attracted. Close to the cathode surface, electron energies are too small to excite atoms/ions, therefore a dark region is formed close to the cathode surface. With increasing distance from the cathode surface, energies of primary and secondary electrons increase, leading to more excitation processes, and a typical *glow discharge* is seen when a plasma is ignited.

Fig. 2.6: Electrical potential distribution of a plasma between cathode on negative potential and anode on ground potential. The positive plasma potential V_p forms between cathode and anode, while an electrically floating object will be at negative floating potential V_f . Potential variations are only observed in sheaths close to walls/objects, while the plasma bulk exhibits a constant positive potential.

2.3. Sputter-deposition

During *physical vapor deposition* (PVD), vapor is created from a solid source that condenses on a surface (i.e., the *substrate*) to form a thin film. PVD techniques are categorized by the way energy for vapor creation is provided: in *evaporation*, thermal energy is transferred, while in *sputtering*, momentum is transferred. Sputtering is extensively used in materials research and industry as it is easy to implement, works for a broad range of materials, and offers access to a wide parameter space for controlling film growth (e.g., temperature, deposition rate, energy of film-forming species). [25]

2.3.1. Diode sputtering

A sputtering device is implemented in vacuum systems by installing two electrodes with high potential difference (in *kV*-range), and introducing a working gas in the chamber. The potential difference leads to partial ionization of the gas and formation of a discharge/plasma. High negative potentials on the cathode lead to attraction of ions that impinge on the surface, hence, the cathode is called *target*. This impingement leads, among others, to target heating (i.e., active target cooling is required) and ejection of target atoms, i.e., the target is *sputtered*. Sputtered atoms are the most common species resulting from ion/target interactions; further species include diatoms, resputtered trapped gas atoms, single ions, reflected incident gas species (backscattered neutrals), and secondary electrons.

Three sputtering regimes exist depending on the energy of the ions impinging on the target (see Fig. 2.7 for schematic illustrations). In the first regime (see Fig. 2.7(a)), incident ions transfer enough energy to a target atom to break all bonds with its neighbors, i.e., single knock-on events occur. The minimum energy for this regime is the *threshold energy* E_{th} for atomic displacement in the target material (typically in the range 2 to 40 *eV*), [4,26] which depends strongly on the nature of the arriving ion, and mass and atomic number of the target atoms. [4] At higher ion energies (0.1 to 10 *keV*), [4] linear collision cascades are formed (see Fig. 2.7(b)), in which a series of atoms in the target transfer the projectile momentum until a surface atom is ejected. This regime is characterized by low collision number densities, so that on average only two particles are moving. [4] A third regime exists for very energetic (*keV* to *MeV*) heavy ions that sputter dense matter (see Fig. 2.7(c)). In this case, the collision number density is high, and many target atoms move at the same time, leading to a local heat spike, i.e., the target melts locally. [27]

The *sputter yield* is the ratio of number of sputtered atoms to incident particles, and is a measure for the efficiency of the sputtering process. Sputter yields vary with particle energy, incidence angle, as well as atomic number and molecular mass of sputtering/sputtered species. [28–30] Depending on these parameters, values for the sputter yield can change over orders of magnitudes, e.g., when argon ions

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impinge on silver with 500 eV, the sputter yield is 3.12, while it is 2.35 for copper targets, and only 0.12 for carbon targets. [4] While the dependence of the sputter yield on the energy of ions is complex (e.g., see Ref. [28]), it can be approximated by a linear function for small energy changes, which is seen in the linear dependency of deposition rate with cathode potential.

Fig. 2.7: Energy regimes of sputtering: (a) single knock-on (low energy), (b) linear cascade, (c) heat spike (high energy).

2.3.2. Sputter gases

Sputter-deposition refers to the synthesis of a film by condensation of sputtered species and is typically performed in argon plasma. Argon is inert (i.e., plasma/film chemical reactions do not have to be considered) and has a high sputter yield with the most common film elements compared to other gases, [30] while being reasonably priced (unlike krypton, xenon, which have higher sputter yields for heavy elements). Neon sputtering results in 20% higher sputter yields than argon for beryllium and carbon, while krypton has a 40% to 60% advantage for elements heavier than tantalum. [30] For compound film growth, reactive gases (e.g., nitrogen, oxygen) are added to the working atmosphere, in combination with elemental or compound targets. It is noted that compound films or multilayers can be also deposited from multiple targets installed in the deposition chamber at the same time.

2.3.3. Magnetron sputter-deposition

The efficiency of the sputtering process is increased by applying a magnetic field $\vec{B}$ perpendicular to the electric field $\vec{E}$ close to the target (i.e., *magnetron sputter-deposition*), as schematically presented in Fig. 2.8. Without magnetic field, electrons are accelerated away from the target, which reduces the occurrence frequency of electron-neutral ionizing collisions. In presence of a magnetic field, electrons (with charge q), are subject to the Lorentz force $\vec{F}_L = q(\vec{E} + \vec{v} \times \vec{B})$, where $\vec{v}$ is the velocity of electrons. $\vec{F}_L$ forces electrons into a helical movement that traps them close to the target, and promotes electron/ion interactions, increasing the plasma density locally, and thus leading to more efficient sputtering of the

target. $\vec{B}$ is typically not strong enough to affect ions that have a much higher mass than electrons. Compared to sputtering without magnetron, magnetized plasmas are stable at lower working pressures (0.1 to 1 Pa) and with lower potentials applied to targets (tens to hundreds of volts). The former leads to higher deposition rates, while the latter decreases substrate heating by energetic electrons.

Magnetron sputter-deposition is further characterized by the way potential (i.e., power) is applied to the target. Power can be applied continuously in a method that is known as direct-current magnetron sputtering. Alternatively, power can be supplied to the target in the form of electrical pulses, also known as pulsed magnetron sputtering. An advantage of the pulsed operation is that the average energy density on a target is not only dependent on the peak power, but also on the fraction of one period that the power is active (i.e., duty cycle). Hence, if the duty cycle is low, much higher power can be applied to targets without risking target overheating. In high power impulse magnetron sputtering, [31,32] very high voltages are applied to the target (700 V to 2 kV for duty cycle up to 10%, with pulse duration in the μs -range), which substantially increases the degree of ionization of the sputtered species. Ionized film-forming species can be accelerated to the substrate by applying a potential (i.e., *substrate bias*), which allows setting the energy range and nature of species arriving at the substrate, i.e., ions offer an additional tool to engineer the morphology of growing films. [33]

Fig. 2.8: Schematic representation of a magnetron sputtering source. Electric $\vec{E}$ and magnetic fields $\vec{B}$, created by applied potential (V) and magnets (N-S), respectively, are indicated by arrows.

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3. Atomic-scale structure-forming processes and growth manipulation

The present chapter describes atomistic processes that lead to the formation of a thin film, and it discusses their manipulation for controlling film morphological evolution. As far as it concerns thin film growth, a distinction between near-equilibrium (i.e., atoms are arranged at minimum-energy configurations) and far-from-equilibrium growth (i.e., kinetic barriers impede thermodynamically favored configurations) has to be made (see Section 3.1). After condensation of atoms on the substrate, surface diffusion and adatom-adatom interactions lead to the formation of isolated islands; these concepts are presented in Sections 3.2 and 3.3, respectively. With continued deposition, islands become larger via processes that are described in Section 3.4. Section 3.5 outlines the film morphological evolution from isolated islands to percolation and continuous film formation, and introduces fundamental properties related to film structure and morphology (e.g., density, texture). By targeted manipulation of these processes, the thin film microstructure—and properties—can be tailored. Concepts for growth manipulation are presented in Section 3.6.

3.1. Near-equilibrium and far-from-equilibrium growth

Thin films are often deposited from the vapor phase, driven by the high supersaturation of atoms in the vapor phase compared to the substrate surface. Per definition, vapor is a gas that can condensate when pressure is increased because its temperature is lower than the critical temperature T_{crit} for gas/liquid phase transition (compared to real/fixed gases, for which the temperature is higher than T_{crit} , e.g., at 300 K, gaseous water is a vapor ($T_{crit,H_2O} \cong 647.1\text{ K}$), and argon is a gas ($T_{crit,Ar} \cong 150.8\text{ K}$)). Sputtering of metal targets at ambient temperature will always create vapors, since critical temperatures of metals range from $\sim 2\,000\text{ K}$ (lead) to $\sim 20\,000\text{ K}$ (rhenium). [34] The driving force for condensation/deposition emanates from the differences of partial pressure of the vapor phase and the vapor pressure created by the liquid/solid phase. Michely and Krug [12] illustrate this for the evaporation of platinum at partial pressure $\sim 10^{-3}\text{ Pa}$ (created at temperature $T_{vapor} = 1900\text{ K}$, resulting in deposition rate $\sim 4.4\text{ nm/s}$) onto a solid platinum substrate at room temperature ($T_{solid} = 300\text{ K}$), which creates a vapor pressure $\sim 10^{-88}\text{ Pa}$. This results in a supersaturation σ_{sup} at the vapor/solid interface

$$\sigma_{sup} = \ln\left(\frac{p(T_{vapor})}{p(T_{solid})}\right) = \ln\left(\frac{10^{-3}\text{ Pa}}{10^{-88}\text{ Pa}}\right) \cong 200. \quad (3.1)$$

Using the σ_{sup} value from Eq. 3.1, the difference in chemical potential of the vapor and solid phase calculates as $\Delta\mu = \sigma_{sup}k_B T \cong 5\text{ eV/atom}$. This large driving force leads to film growth far from thermodynamic equilibrium, such that film formation is

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governed by the kinetic rates of atomic-scale processes. Despite the latter, equilibrium growth arguments are frequently used in the literature, as they provide a physically correct description of the asymptotic evolution of film morphology.

One of the most widely used near-equilibrium classifications of film morphology is that of Bauer, [35] which treats the case of epitaxial growth. According to Bauer, film morphology is governed by the interplay among the surface energies of the substrate γ_s and the film γ_f , and the film/substrate interface energy γ_i . When $\gamma_s \geq \gamma_f + \gamma_i$, which is typical for epitaxial growth, energy minimization arguments require that the film wets fully the substrate, and growth occurs in a layer-by-layer fashion (Frank-van der Merwe growth mode, Fig. 3.1(a)). This growth mode is also seen for homoepitaxy (i.e., film and substrate are chemically and crystallographically identical), where $\gamma_i = 0$, and thus $\gamma_s = \gamma_f$.

For $\gamma_s < \gamma_f + \gamma_i$, the energy of the film/substrate system is minimized by maximizing the exposed substrate surface, such that film material forms three-dimensional (3D) mounds/islands. This growth mode, depicted in Fig. 3.1(b), is called Volmer-Weber growth. If the lattice parameter of substrate and film differ, as commonly seen in heteroepitaxial growth (i.e., film and substrate differ both chemically and crystallographically), the film material grows pseudomorphically (i.e., with the lattice parameter imposed by the substrate), and strain builds up to accommodate the lattice mismatch. In this case, an additional energy component has to be considered, the elastic strain energy γ_{el} , which increases with film thickness. During Stranski-Krastanov growth (Fig. 3.1(c)), initially, $\gamma_s > \gamma_f + \gamma_i + \gamma_{el}$, and a wetting layer forms, but at a critical thickness $\gamma_f + \gamma_i + \gamma_{el}$ becomes larger than γ_s , and mounds form on the wetting layer to relieve the strain. Alternative strain-relief mechanisms include the formation of dislocations or surface undulations. [36,37]

Fig. 3.1: Schematic representation of near-equilibrium film growth modes; (a) layer-by-layer growth (Frank-van der Merwe mode), (b) island formation (Volmer-Weber mode), and (c) island formation on wetting layer (Stranski-Krastanov mode).

Epitaxial growth necessitates that the substrate is a single crystal. The latter may not always be the case—e.g., during deposition on polycrystalline substrates, amorphous materials, and polymers—which yields polycrystalline films, i.e., films composed of grains with different crystallographic orientations, separated by grain boundaries. While the Bauer criteria were not derived for polycrystalline systems, they are still applicable for describing local epitaxial growth at the length scale of individual grains.

As explained at the outset of the present section, film growth proceeds far from equilibrium, such that film morphological evolution is largely governed by the kinetic rates of atomic migration (diffusion) processes. The occurrence rates of these

processes are determined by the potential energy landscape that atoms encounter as they transverse on the film growth front. The following sections describe important atomic processes during non-equilibrium film growth and explain the way by which their kinetic rates affect film morphological evolution.

3.2. Adatom diffusion

During thin film deposition from the vapor phase, atoms arriving at the substrate surface have broad energy distributions, which they dissipate into the substrate lattice before being adsorbed, so that they become *adatoms*. Independent of the substrate surface (e.g., atomically flat, with (vicinal) steps, rough) different adsorption sites exist, distinguished by varying numbers of (next-) nearest neighbors (see Fig. 3.2(a)), and a net flux of adatoms to energetically favorable adsorption sites may form. To diffuse by hopping to low-energy sites on an atomically flat substrate, adatoms have to overcome energy barriers E_D separating surface sites, created by the periodic surface potential landscape formed by substrate atoms, which is illustrated in Fig. 3.2(b). Successful hopping events yield a two-dimensional (2D) adatom random walk on the surface, described by the surface diffusivity D ,

$$D = D_0 \exp\left(-\frac{E_D}{k_B T_S}\right), \quad (3.2)$$

where k_B and T_S are the Boltzmann constant and substrate temperature, respectively. The prefactor D_0 is approximated as $D_0 = a^2 v_0 / 4$, with the minimal adatom translational hopping distance a , the attempt frequency v_0 ($\sim 10^{12}$ Hz). The factor $1/4$ is a convention used for 2D diffusion; generally, a prefactor $1/(2n)$ is used for n -dimensional diffusion. [12]

While E_D accounts for energy barriers for diffusion on flat surfaces, preexisting morphological features can lead to local variations of this value. A common feature on substrate surfaces are steps between terraces that add an additional barrier—called Ehrlich-Schwoebel barrier E_{ES} —for diffusion across the step. This additional barrier stems from the lower coordination number of adatoms during the step-edge crossing, and breaking of bonds, as indicated in Fig. 3.2(a) and (b). The total step-edge barrier E_{SE} calculates as $E_{SE} = E_D + E_{ES}$, and adatoms need higher energies to overcome it than for diffusion on a flat surface. Concurrently, the step represents a low-energy position on the lower terrace, where the coordination number is maximum; up-stepping is therefore associated with very high energy barrier and is an unlikely process in classical epitaxial growth theory.

Fig. 3.2: (a) Adatom on top of a terrace (dark gray circle). Striped positions indicate high-energy position while down-stepping (left) and low-energy position at the kink site (right). (b) Potential energy landscape experienced by the adatom in (a) when diffusing. While on the flat terrace, the energy barrier E_D has to be overcome, when stepping over the edge, the adatom encounters a large step-edge barrier E_{SE} . (c)-(f) Illustrations of growth modes depending on surface diffusion and step-edge crossing rates, as determined by E_D and E_{SE} ; (c) step flow growth, (d) layer-by-layer growth, (e) mound formation, and (f) self-affine growth.

The effect of atomic diffusion rates (mediated by the energy barriers) on the film morphology can be illustrated by homoepitaxial growth, for which thermodynamics (i.e., the Bauer classification) predicts layer-by-layer growth. If adatoms can migrate on the terraces and descend step-edges without restriction (i.e., unlimited *interlayer transport*), while the mean separation between islands (i.e., nucleation length) is longer than the average terrace length, adatoms diffuse and bond to the low-energy site at the terrace edge. This leads to *step flow* growth, where the terrace number density remains constant, as illustrated in Fig. 3.2(c). If the nucleation length is smaller than the average terrace length, nucleation of islands may occur on terraces (see Section 3.3 for a description of the nucleation process), but since step-descent is unlimited, the bottom layer will be completed before second-layer islands form, and *layer-by-layer* growth occurs (see Fig. 3.2(d)). In case of kinetically limited step-edge descent, the residence time of adatoms on terraces increases, such that second-layer nucleation occurs, leading to *formation of 3D mounds* (illustrated in Fig. 3.2(e)). When both terrace diffusion and, all the more, step-edge crossing are kinetically restricted, adatoms largely remain on their condensation site (see Fig. 3.2(f)). This yields to the so-called *self-affine* growth which is characterized by film porosity, surface roughness, and self-similar morphology.

3.3. Island nucleation

Residence times of adatoms on surfaces are limited by desorption (e.g., at high T_s), bonding to existing structures (e.g., steps, islands), or nucleating of new islands. [4] The latter is the principle adatom loss mechanism during initial growth stages on an atomically flat surface. In course of the random surface walk, adatoms can meet, and form *nuclei*. The size of a nucleus is equal to the number of atoms i in the nucleus. Clusters are thermally stable when $i > i^*$, while they dissolve if $i < i^*$. In many film/substrate systems, $i^* = 1$ has been found, [38] i.e., diatomic clusters are stable, and will, on average, grow in size as deposition continues. Stable clusters are referred to as *islands*, and the island number density N increases during the initial growth stages (i.e., transient nucleation regime). As N increases, adatom incorporation into islands becomes more probable, leading to a reduced number of adatoms on the surface that can nucleate new islands, and a steady-state island number density N_{sat} is reached that scales as

$$N_{sat} \sim \left(\frac{F}{D}\right)^\chi. \quad (3.3)$$

In Eq. 3.3, F is the deposition rate, and χ is a scaling exponent that depends on i^* and the dimensionality of the growing islands. In weakly-interacting film/substrate systems, 3D islands form, [2,39,40] and for $i^* = 1$, $\chi = i^*/(i^* + 2.5) = 2/7$. [38] N_{sat} is a quantity that strongly impacts film growth at later growth stages, as it sets the frequency of islands-island interactions (see Section 3.4); for large values of N_{sat} , the average island spacing is small, and islands interact early, while for low values, islands are further apart and have to grow considerably in size before interacting. During growth manipulation studies, changes in N_{sat} are therefore investigated (see Section 3.6).

In Section 3.2, the concept of second layer nucleation was briefly mentioned, i.e., the nucleation of an island on an existing island. This process is responsible for the formation of 3D mounds on surfaces that lead to roughness build-up at the film growth front. Nucleation of islands occurs, if the adatom density is sufficiently high. For a discussion of second layer nucleation, the characteristic time of adatom arrival (i.e., condensation from the vapor phase) is compared to adatom residence times on an island (i.e., dependent on island size, E_{SE}). If the adatom residence time is much shorter than the time between consecutive adatom arrivals, second layer nucleation is not possible. This is the case for small island sizes (e.g., at early film formation), and low values of E_{SE} .

3.4. Island growth mechanisms

During initial film growth stages, islands grow through incorporation of adatoms on the substrate surface. As the substrate area coverage by film material increases, direct deposition onto islands becomes more probable, but does not play a major role, as surface coverages are low in general. When islands grow further, their average distance decreases, and island-island interactions become the dominant island growth mechanism, as explained in the following sections.

3.4.1. *Island coalescence*

Coalescence is an island growth mechanism that becomes active, once two islands are very close to each other (i.e., they are separated by a gap of several atom diameters). At this point, it becomes energetically favorable to form an island/island interface (i.e., grain boundary), and close the gap by elastically straining the islands. This process is called *impingement*, and initiates *coalescence* (i.e., reshaping of the island cluster until equilibrium shape is reestablished), which is driven by the minimization of the surface energy. The reshaping of the island cluster, schematically presented in Fig. 3.3, commences at the neck, which is a concave surface, offering a higher number of nearest neighbors to arriving atoms compared to convex surfaces. This results in a net flux of atoms toward the neck and closing thereof, while the mass centers of the two coalescing islands approach each other. Coalescence is completed, when an equilibrium shape is reestablished, the grain boundary has been eliminated, and a single crystallographic orientation is present in the island. In case of different island crystallographic orientations before impingement, islands may need to rotate for completing the process. Moreover, coalescence leads to a bimodal distribution of island sizes, as after coalescence completion, the substrate surrounding the newly formed island is void of material, which enables *secondary nucleation*.

According to the sintering theory, in the case of two hemispherical islands with radius R , the time τ_{coal} for coalescence completion is $\tau_{coal} \cong R^4/B$, [41] where B is the coalescence-rate parameter that scales with the adatom surface self-diffusivity (i.e., is temperature dependent). Island coalescence is initially very fast (i.e., droplet-like coalescence), but becomes slow with increasing island size, and can eventually not be completed before another island impinges on the coalescing island pair. In this stage of *incomplete coalescence*, islands have elongated shapes, and may be polycrystalline. This is an important step toward continuous film formation, which is further discussed in Section 3.5. In the course of coalescence, the film morphology set during island nucleation is changed, and the newly formed morphology is largely dependent on τ_{coal} . Manipulation of coalescence rates is therefore a pathway to morphology tailoring.

Fig. 3.3: Schematic representation of impingement and coalescence of two islands (top view). As coalescence progresses, the mass centers of the islands approach, and material is transported from convex to concave surfaces, indicated by arrows. Coalescence is completed when an equilibrium shape is reestablished.

3.4.2. Ostwald ripening

Atoms on island surfaces are weaker bonded than bulk atoms and can therefore detach from the islands. In case of stable islands, the ratio of detachment to reattachment processes is in favor of reattachment processes, i.e., on average, the island size does not decrease. The chemical potential $\mu = 2\Omega\gamma/R$, where Ω is the atomic volume, is associated with this “escaping tendency”. [4] Comparing island sizes, μ is large for small islands, resulting in weaker bonded surface atoms (i.e., larger surface curvature, fewer nearest neighbors), and concurrently, small islands have a large adatom cloud surrounding them compared to larger islands (see Fig. 3.4). When two islands with different sizes are close to one another, the adatom clouds overlap, and adatoms that detach from the small island have a higher probability to attach to the larger island than reattaching to the smaller one. [42] This tendency can also be expressed as differences in adatom number densities surrounding the islands that lead to diffusion of adatoms from the high-number density region close to the small island to the low-adatom-density region surrounding the large island. Ostwald ripening is only active if adatom number density gradients are present, [43] it is therefore not active during film deposition from the vapor phase, where a constant influx of newly formed adatoms leads to a uniform high adatom density, and the gradient disappears. Ripening can be the dominant growth mechanism in non-continuous films after deposition has stopped.

Fig. 3.4: Illustration of adatom number densities surrounding two islands of different size. The small island is surrounded by a larger adatom number density compared to the large island, resulting in a density gradient, and adatom diffusion.

3.4.3. *Smoluchowski ripening*

Islands are typically considered immobile, but at conditions of high atomic mobility, islands can execute concerted diffusive motion. This has been observed for small islands, islands with “magical numbers” in homoepitaxy, [44] and very large islands that support internal vibrations, and are therefore incommensurate with the substrate. [45–47] Mobile islands can impinge on stationary islands, and coalesce, leading to increased island size and decreased island number density. This process is referred to as Smoluchowski ripening.

3.5. Elongation, percolation, and continuous film formation

During initial growth stages, film morphology is characterized by isolated islands with (near-) equilibrium shape that grow in size via processes presented in Section 3.4, out of which island coalescence is the most prominent during deposition from the vapor phase. When coalescence of an island-pair cannot be completed before impingement of a third island, the equilibrium shape cannot be attained. Hence, islands obtain elongated shapes (which can be approximated by ellipses in top-view), characterized by an in-plane aspect ratio—the ratio of major to minor ellipse axis—larger than unity. This point in growth is called elongation transition.

The *elongation transition thickness* θ_{elong} is a characteristic quantity that describes early film formation, and its scaling with deposition rate F and substrate temperature T_s gives valuable information about the dynamic competition of structure-forming processes (island nucleation vs. coalescence). [48–50] While θ_{elong} is readily obtainable in simulations (i.e., thickness at which the average island cluster consists of two islands), experimental determination is difficult, as it does not have implications to measurable physical properties. While visual observation of film surfaces close to θ_{elong} , e.g., with scanning tunnel microscopy, [51,52] is one option to study this transition, an indirect approach has been proposed by Lü *et al.*, [53] who determine θ_{elong} by changing the adatom arrival rate during deposition and thus activating/freezing island coalescence.

Morphological transitions at higher film thicknesses can be determined experimentally easier because they impact film physical properties. With continued deposition beyond elongation transition, the rate of island impingement increases, and an interconnected array of film islands is formed on the substrate surface; this transition occurs at the *percolation thickness* θ_{perc} . In case of conductor deposition on insulating substrates, the film becomes macroscopically conductive at θ_{perc} , and film resistivity decreases several orders of magnitude. [54–56]

3.5 Elongation, percolation, and continuous film formation

The formation of a continuous film requires the holes between interconnected islands in the percolated structure to be filled. With increasing amount of deposited material, the substrate coverage increases, such that direct deposition of film atoms into holes becomes less probable. For very narrow holes, atom trajectories are affected by the surrounding 3D islands, resulting in atom adsorption on the island facets (i.e., steering). [57] Concurrently, hole-filling requires adatom diffusion to the bottom of the hole via step-edge descent. In polycrystalline films, where grains are separated by grain boundaries (GB), the presence of the step-edge barrier E_{SE} (see Section 3.2) leads to mound formation as explained in the following (also known as Zeno effect): [57,58] Adatoms that are deposited onto a terrace diffuse to the ascending step, if they cannot cross the step-edge because of E_{SE} . Terrace growth is stopped at GBs; consequently, terrace length decreases as the ascending step approaches the GB, and the number of deposited adatoms decreases, which stops the step progression. For small terrace lengths (~ 5 atoms), the Ehrlich-Schwoebel barrier E_{ES} collapses, [57,59] and fast mass transport toward the GB (i.e., *downward funneling*) closes the remaining gaps.

Knowledge of the *continuous film formation thickness* θ_{cont} of films is important to ensure that the substrate surface is covered completely by film material. Additionally, many of the morphological features and properties of the film are set by the time a film becomes continuous. In the following, the most important of these properties are listed and explained.

Mass density

The mass density ρ_m of a thin film is equal to the bulk density of the film material, if the chemistry is identical (i.e., no composition gradients) and no porosity has formed. Film porosity forms, when adatom mobility is not sufficient on the surface (compare self-affine growth in Fig. 3.2(f)), or shadowing effects occur, e.g., during deposition at glancing incidence. [4] Film density can be determined, e.g., via x-ray reflectometry (XRR, see Section 5.3.6). Density fluctuations are also visible in scanning electron microscopy (SEM, see Section 5.3.2) and transmission electron microscopy (TEM, see Section 5.3.3).

Grain size

The grain size determines opto-electronic properties, e.g., conductivity, and mechanical properties of a film (e.g., stress-state). Cross sectional SEM and TEM (Sections 5.3.2 and 5.3.3) can be used to determine if grains are columnar, V-shaped or globular, while x-ray diffractometry (XRD, see Section 5.3.5) and electron backscatter diffractometry (EBSD, see Section 5.3.4) give information about the out-of-plane and in-plane grain size, respectively.

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Surface roughness

Knowledge of the surface properties of a thin film is essential to determine its interaction with its environment. It is largely determined by the surface mobility of adatoms. The root-mean-square roughness w is a quantity that can be determined from atomic force microscopy (AFM, see Section 5.3.1), and is a fitting parameter for XRR data (see Section 5.3.6)

Texture

In case of polycrystalline growth, initially, islands nucleate with random crystallographic orientations, which grow with different speed, due to thermodynamic reasons (surface energies of densely-packed atomic planes are lower than for loosely-packed planes), or kinetic reasons (planes with high diffusion barrier E_D host many adatoms that can nucleate into islands, while a low E_D leads to low adatom density, and concurrently, to few nucleation events). [60] Islands that grow fast can overgrow other islands that grow slower, and a texture develops, i.e., a crystallographic orientation is overrepresented in the polycrystalline film. Texture can continue to evolve as film thickness increases, and kinetic limitations arise (e.g., due to surface roughness). Texture analysis is performed by XRD (see Section 5.3.5) or EBSD (see Section 5.3.4).

3.6. Influence of process parameters on microstructural evolution

The nanoscale processes that lead to the formation of a thin film can be altered by changing process parameters. Concurrently, the morphology of a growing film is determined by these parameters, which are often interdependent. For use of thin films in applications, specific morphological features (e.g., low surface roughness, low level of contamination) may be required, and by understanding how process parameters affect the film growth, morphology manipulation methodologies can be devised to achieve them.

3.6.1. *Temperature*

Changes in the deposition temperature affect the mobility of (ad)atoms during film growth, e.g., the diffusivity increases (see Eq. 3.2) as energy barriers (E_D) can be overcome more easily. For many diffusion processes (e.g., lattice, grain boundary, or dislocation diffusion) and materials, the relation $E_D = c T_m$ is valid, [4] where c is a diffusion process dependent constant, and T_m is the bulk melting temperature of the film material. Substituting E_D in Eq. 3.2 leads to $D \sim \exp(-c T_m / (k_B T_s))$. Consequently, the homologous temperature $T_H = T_s / T_m$ (temperatures in Kelvin) is a parameter for a general comparison of mobilities among various film materials.

Common film morphological features can be found for similar values of T_H : [3] In the low mobility regime $T_H < 0.2$, neither bulk nor surface diffusion are active, and porous, columnar grains with small diameter (i.e., $\sim 1 - 10 \text{ nm}$) form. In the intermediate mobility regime $0.2 < T_H < 0.4$, surface diffusion is active, while energy barriers for bulk diffusion cannot be overcome. This leads to competitive grain growth, and fast-growing grains overgrow slow grains, which results in a V-shaped grain structure. For high mobility (i.e., $T_H > 0.4$), where surface and bulk diffusion are active, columnar grains form, with dense grain boundaries that are perpendicular to the substrate surface. With active bulk diffusion, grain growth throughout the whole film thickness is possible, leading to grain size that increases with increasing film thickness, and highly textured films.

This correlation between film morphology and homologous temperature led to the development of *structure zone diagrams*, [3,61] which allow for qualitative prediction of film morphology as a function of deposition parameters. Originally conceived for evaporated films, structure zone diagrams were expanded to account for the energy of arriving particles during sputter-deposition, [62–65] and the role of contamination on the morphological evolution. [66]

In Section 3.3, the scaling of the saturation island number density N_{sat} with deposition rate and diffusivity was presented (see Eq. 3.3). With increasing values of T_s , adatom diffusivity increases, and island nucleation events on a flat surface occur less often, i.e., N_{sat} decreases. Concurrently, a film deposited at high T_s can

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be expected to show a larger average grain size. This trend is independent of grain growth, activated by bulk diffusion.

Island coalescence is a surface self-diffusion dependent process, and therefore promoted by increased value of T_s . Faster coalescence completion shifts the elongation transition, and consequently percolation and continuous film formation, to occur at larger thicknesses, leading to a strongly coalescence-controlled film morphology.

3.6.2. *Deposition rate*

The deposition rate F represents the vapor arrival rate at the substrate, and is set by the rate of plasma ions impinging on the target surface (i.e., determined by the electric potential on the target), the sputter yield of the target material (i.e., number of target atoms that are sputtered per impinging working gas ion), as well as working gas and pressure (see Chapter 2 for more details). A high value of F signifies that a high number of atoms arrive per substrate surface unit during a given time unit, and island nucleation events occur often, i.e., N_{sat} increases with increasing F . It is noted that the F -dependence of N_{sat} is much weaker than its T_s -dependence (see exponential function in Eq. 3.2), and F has to be decreased by orders of magnitudes to match the N_{sat} decrease set by increasing T_s few Kelvin.

Vacuum conditions in a film deposition chamber are not ideal, i.e., residual gases (e.g., oxygen, nitrogen, water) are present that contaminate the growing film. A comparison of F with the monolayer formation time τ_{ML} from the background pressure allows estimations of the contamination level of the growing film (see Section 2.1.2). For high values of F , contamination arrival becomes less significant, and cleaner films are grown. The most direct way to increase F is applying a higher power to the target to increase the number of arriving plasma ions. Concurrently, more energy is introduced to the target that needs to be removed via cooling, otherwise the target is overheated, leading to cracking, and/or melting.

3.6.3. *Working pressure*

A working gas is introduced into a deposition chamber to create a plasma, and initiate sputtering of the target. The pressure of the working gas largely determines the mean-free path of atoms in the chamber during the sputter-deposition process. At high working pressure, target atoms collide with working gas atoms often, and lose energy with every collision. Consequently, the average energy of atoms arriving at the substrate surface decreases with increasing working pressure.

The energy of arriving species on the substrate is instrumental in the texture evolution of the growing film, i.e., high-energy atoms promote surface rearrangement processes. [33,67] Deposition profile and rate, as well as energy

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and direction of sputtered particles can be simulated with the Simulation of the Metal Transport (SiMTra) Monte Carlo program. [68] It simulates the transport of sputtered particles through the working gas considering binary collisions, and the user can implement the experimental setup (e.g., chamber dimensions).

3.6.4. *Minority species*

Alloying is one of the oldest material engineering strategy that allows changing optical, mechanical, and electrical properties of a material. In thermodynamic equilibrium, the interaction of host material and minority species can be determined by calculating the Gibbs free energy of mixing $\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$, where $\Delta_{mix}H$ and $\Delta_{mix}S$ are enthalpy of mixing and configurational entropy, respectively, and T is the system temperature. [53] $\Delta_{mix}S$ is strongly dependent on the composition of the compound, e.g., in a binary compound A_xB_{1-x} , the configurational entropy is $\Delta_{mix}S = -nR[x \ln(x) + (1-x) \ln(1-x)]$, where n is the total number of moles, R is the gas constant, and x is the mole fraction. From $0 < x < 1$ follows that $\ln(x)$ and $\ln(1-x)$ are always negative, consequently, $\Delta_{mix}S > 0$, and leads to a decrease in $\Delta_{mix}G$. For negative values of $\Delta_{mix}G$ in system consisting of elements A and B, the system is *miscible*, i.e., energy is minimized by forming a maximum of A-B bonds, and the species intermix spontaneously. An example for a miscible binary system is Ag-Au, which are miscible in the solid and liquid states. If $\Delta_{mix}G$ is positive, elements are *immiscible* and phase separation occurs below the miscibility gap, e.g., Ag is immiscible with Ni and Cu in the solid phase.

Thermodynamic equilibrium considerations alone cannot explain phase formation during thin film growth from the vapor phase, where metastable phases can form due to kinetic limitations of the structure-forming species (see Section 3.1). If the system is thermodynamically immiscible, phase separation occurs, if atoms have enough energy to diffuse, and one element *segregates*. In case of no chemical bonding to the film material, and efficient segregation of the minority species, such that it remains at the growth front at all times, the term *surfactant* is used. [12] Surfactants are used to manipulate film morphology as they affect both energetic and kinetic aspects of the film growth front. In the case of homoepitaxy, three different ways by which surfactants allow for growth manipulation have been identified in the literature:

- (i) The surfactant changes the diffusion barrier E_D , e.g., exposing Pt(111) surfaces to oxygen increases E_D , and results in a larger island nucleation density in the Pt/Pt(111) system. [70] Concurrently, an increase in E_D promotes layer-by-layer growth.
- (ii) The step-edge barrier E_{ES} is influenced by the presence of a surfactant, e.g., carbon monoxide preferentially adsorbs on step-edges of the Pt(111) surface, and thus increases E_{ES} . [71] This promotes mound formation in the Pt/Pt(111) system.

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- (iii) In a third scenario, the presence of surfactants changes the adatom diffusion along step-edges, and thus can lead to a change from compact to ramified island shapes. This increases the ratio of sites at the step-edge vs. terrace sites, and the attempt frequency of adatom step-edge crossing increases. Consequently, the lifetime of adatoms on the terrace and the second-layer island nucleation probability decrease. Sb surfactants have this effect on Ag/Ag(111) growth, [72] and shift the film growth mode from mound formation to layer-by-layer growth.

The film formation mechanisms in weakly-interacting film/substrate systems are different from those in strongly-interacting epitaxial systems, and depend strongly on the complex interplay of island nucleation, growth and coalescence. [3,5,7,73] Growth manipulation by surfactants is less well studied in these systems, however, empirical studies show that surfactants can suppress the uncontrolled formation of a 3D morphology, e.g., oxygen and nitrogen increase the island nucleation density, and improve wetting of Ag and Cu films on oxide substrates, promoting a 2D film morphology. [74–80]

4. Stress generation and evolution during thin film growth

During far-from-equilibrium thin film deposition, atoms often arrange themselves in metastable configurations, resulting in formation of mechanical stress that can lead to failure of thin film components and devices, e.g., via delamination, crack formation, buckling. The presence of a substrate upon which films are deposited yields different types of stresses (thermal stress, coherency stress, intrinsic stress), which are briefly explained in Section 4.1. The present thesis focuses on intrinsic stresses, which can, depending on deposition conditions, be tensile or compressive. Moreover, intrinsic stresses typically evolve with film thickness in a way that is related to the various formation stages discussed in Chapter 3: During island formation and growth, the Laplace-pressure-reduced lattice constant results in compressive stress (Section 4.2), while tensile stress emerges in coalescing island pairs (Section 4.3). The stress sign after continuous film formation depends on the mobility of adatoms on the film surface, as well as on the microstructural evolution (e.g. grain size, texture) of the continuous film during growth, as explained in Section 4.4. After deposition interruption, stress that has formed in the film can continue to evolve, which is discussed in Section 4.5. Finally, Section 4.6 summarizes some of the most established models that allow for calculation of stress formation and evolution during film growth.

Stress data discussed in this chapter are presented in film force per unit width (usually abbreviated as film force) vs. film thickness (h_f) diagrams, or stress-film thickness product ($\sigma \times h_f$) vs. h_f diagrams. Film force and $\sigma \times h_f$ are equivalent quantities and have the unit N/m . Data is interpreted as described in the following: The *average film stress* is tensile if the film force is positive; concurrently, the average stress is compressive for negative film force. The slope of film force vs. h_f data corresponds to the *incremental stress*, i.e., the stress that forms in the film due to growth of an additional layer of the film. Details about the generation of *in situ* stress data are given in Section 5.2.2.

4.1. Classification of stresses in thin films

Mechanical stress observed during far-from-equilibrium film growth may have different origins. This section outlines three stress generation mechanisms: (i) thermal stress σ_{th} due to the mismatch between thermal expansion coefficients of substrate and film; (ii) coherence stress σ_{coh} due to imposition of a crystal lattice constant different from the equilibrium value by the substrate in epitaxial film growth; and (iii) intrinsic stress σ_i that results from the film microstructural evolution during film growth.

4 Stress generation and evolution during thin film growth

4.1.1. Thermal stress

The temperature at which films are deposited may differ from their application temperature. For instance, transition metal nitride coatings—used to protect the surface of cutting tools—are grown at $\sim 600\text{ K}$ to ensure sufficient atomic mobility for forming dense microstructures, they are stored at room temperature, and they are operated at temperatures exceeding $\sim 900\text{ K}$. Upon such temperature variations ΔT_s , relative to the synthesis temperature, both film and substrate dimensions change (i.e., contract or expand), the magnitude of which depends on the respective thermal expansion coefficients of substrate ($\alpha_{th,s}$) and film ($\alpha_{th,f}$). Usually, a mismatch $\Delta\alpha_{th} = \alpha_{th,s} - \alpha_{th,f}$ exists, resulting in the buildup of thermal stress σ_{th} . For a homogeneous film on a rigid substrate, σ_{th} is calculated as $\sigma_{th} = Y_f \Delta\alpha_{th} \Delta T_s$, where Y_f is the biaxial modulus of the film. Thermal stress can be compressive or tensile, depending on the film/substrate system (i.e., the thermal expansion difference $\Delta\alpha_{th}$), and can reach higher values than the film's yield strength, leading to plastic deformation and/or film damage. [74,75]

In addition, even in the absence of intentional heating, the substrate temperature can rise during film growth due to the impingement of energetic particles from the arriving vapor flux. [4] This uncontrolled heating is pronounced for high deposition rates, long deposition times, and growth conditions for which species arriving at the substrate have high energies (e.g., when a bias voltage is applied on the substrate, and at low working pressure). Compared to intentional heating during film growth, the temperature induced by atom impingement is in most cases small (i.e., tens of Kelvin), but for precise analysis of stress evolution even such small temperature changes need to be considered.

4.1.2. Coherency stress

In heteroepitaxial growth, films are deposited onto structurally and chemically different single-crystalline substrates, which impose a crystal structure (substrate lattice constant a_s) on the film lattice (film lattice constant a_f). Hence, films may grow *pseudomorphically*, i.e., with a lattice constant that is different from their equilibrium lattice constant. The lattice misfit leads to formation of coherency strain defined as

$$\varepsilon_{coh} = \frac{a_s - a_f}{a_f}, \quad (4.1)$$

which manifests itself as coherency stress $\sigma_{coh} = \varepsilon_{coh} Y_f$, where Y_f is the film biaxial modulus. Following Eq. 4.1, σ_{coh} is compressive for $a_s < a_f$, and tensile for $a_s > a_f$.

An example of coherency stress formation is given in Fig. 4.1, where the evolution of film force per unit width vs. film thickness is presented for Fe evaporation onto MgO(100) substrates for various deposition temperatures. [83,84] Fe grows

4.1 Classification of stresses in thin films

epitaxially on MgO (epitaxial relationship $\text{Fe}(001) \parallel \text{MgO}(001)$ and $\text{Fe}[001] \parallel \text{MgO}[110]$), which leads to a lattice misfit of $\varepsilon_{coh} = 3.5\%$ at 500 K, and a theoretical $\sigma_{coh} = 6.8 \text{ GPa}$, as represented by the dashed line in Fig. 4.1. Koch *et al.* [83] found that for deposition at 500 K, the stress is close to the theoretical value σ_{coh} up to a film thickness of $\sim 8 \text{ nm}$, after which it levels off. At 500 K, the film grows in a layer-by-layer fashion, such that the maximum theoretical σ_{coh} is formed and strain energy is stored in the film until reaching a critical thickness, above which strain and stress are relieved, and the total energy of film/substrate system is minimized via nucleation of misfit dislocations. With decreasing deposition temperature to 465 and 440 K, nucleation of misfit dislocation and stress relief occur at smaller thicknesses. Further decrease of the temperature to 360 K yields growth conditions during which atomic mobility is insufficient for nucleation of misfit dislocations, such that tensile stress that is lower than σ_{coh} builds up during film growth.

Fig. 4.1: Evolution of film force per unit width vs. film thickness during evaporation of Fe films onto MgO(001) substrates at different substrate temperatures. The dashed line indicates the maximum misfit stress for epitaxial growth. Reprinted with permission from Ref. [84].

Another example is the heteroepitaxial system Ge/Si(111), in which stress is partially relieved by creating three dimensional (3D) islands, i.e., via the Stranski-Krastanov growth mode (see film force vs. thickness measurements in Fig. 4.2). In this work by Koch *et al.* [78], Ge is grown on Si(111) substrates via molecular beam epitaxy (MBE), i.e., an evaporation technique that leads to epitaxial films with high purity, and the film force per unit width is measured *in situ*. The lattice misfit between film and substrate at $T_s = 915 \text{ K}$ leads to $\varepsilon_{coh} \cong -4\%$, and $\sigma_{coh} = -6.7 \text{ GPa}$. The data in Fig. 4.2 shows that a compressively strained film forms up to a film thickness $\sim 0.7 \text{ nm}$ on the Si substrate (stress regime I), which corresponds to $\sim 2.5 \text{ monolayers (ML)}$ of Ge(111) that wet pseudomorphically the substrate. At larger film thicknesses, less compressive stress forms in the Ge film (i.e., lower slope in regime II in Fig. 4.2), due to partial relief of stress by formation of 3D islands. [85] The observed stress in regime II stems from formation of misfit dislocations and stacking faults in the islands.

4 Stress generation and evolution during thin film growth

It is noted that the 3D structures that form in epitaxial semiconductor films are known as Asaro-Tiller-Grinfeld instabilities. [36,37,86] These instabilities form spontaneously on the surfaces of strained crystals to elastically relax stress on the additionally created surface.

Fig. 4.2: Evolution of film force per unit width vs. film thickness during growth of Ge films on Si(111) substrates at different substrate temperatures. Regimes I and II correspond to formation of an epitaxial wetting layer and 3D island formation, respectively. The dashed line indicates the maximum misfit stress for epitaxial growth. Reprinted with permission from Ref. [85].

4.1.3. Intrinsic stress

Intrinsic stress forms due the microstructural evolution of thin films during growth, and it is a result of the far-from-equilibrium nature of vapor-based film deposition techniques. Like thermal and coherency stress, the nature of the substrate has influence on the intrinsic stress, as the interaction of film atoms and substrate surface largely governs the film morphology: While a flat surface morphology is expected for strongly-interacting film/substrate systems, 3D growth is seen in weakly-interacting systems. [7] For the latter case, film morphology develops from isolated islands, via coalescing island clusters, to a continuous film. These growth stages lead to a characteristic stress evolution that is discussed in greater detail in Sections 4.2 through 4.6.

4.2. Stress during island formation and growth

Stress formation during early film growth stages, where isolated islands populate the substrate (i.e., nano particles), results from two effects: the Laplace-pressure-reduced lattice parameter in nanoscale objects, and the decreasing atom mobility with increasing particle size. This section describes these two concepts briefly, and connects them to stress generation.

Film formation commences with the nucleation of islands on the substrate surface. These nano-sized structures can be approximated as hemispheres with radius r . The existence of stable islands dictates a balance between the force exerted by the curvature of the surface (i.e., the surface stress f) and the force due to the pressure p in the hemisphere, which can be expressed as [87,88]

$$\pi r f = \frac{1}{2} \pi r^2 p. \quad (4.2)$$

In general, the surface stress f_{ij} is a tensor, where j denotes the direction in which the force acts, and i denotes the direction of the surface normal. For metal surfaces with low Miller indices, $f \cong 1 \text{ N/m}$, i.e., f is positive and of the same order of magnitude as the surface energy γ . [89] For (incompressible) liquids, $f = \gamma$, and the expression “surface tension” is often used for both quantities. This is not true for solids, where f might be negative, depending on how atoms are rearranged on the surface. A distinction between surface stress and surface energy is therefore essential for solids.

Rewriting Eq. 4.2 gives $p = 2f/r$, where p is the Laplace pressure. Assuming that islands are crystalline with a cubic lattice (with lattice constant a) and using the compressibility $K = -\Delta V/(pV)$, we find

$$\frac{\Delta a}{a} = -\frac{2}{3} \frac{K}{r} f, \quad (4.3)$$

where Δa is the change in lattice constant due to the surface stress f . According to Eq. 4.3, the lattice constant in a nano particle decreases due to surface stress (if $f > 0$), and this decrease becomes less pronounced with increasing particle size, i.e., in a particle with infinite radius no surface stress-induced lattice decrease is expected. This dependency between particle size and lattice constants has been verified experimentally, see e.g., the work by Mays *et al.* [88] on lattice constant evolution of evaporated gold nano particles. Figures 4.3(a)-(c) present schematically the evolution the lattice constant of a metallic nano particle with increasing particle size (only one dimension indicated for clarity).

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Fig. 4.3: Evolution of lattice constant a and melting temperature T_m of a supported nano particle with increasing particle size. Lattice constants in schematics (a) through (c) are equilibrium values, while in (d), atom mobility is too low and the smaller lattice constant a_2 is inherited, leading to compressive stress.

Nanoscale particles do not only have smaller-than-bulk lattice constants, but also a melting temperature T_m that is lower than the bulk value. [90] The latter results from the high surface-to-volume ratio of nano objects. Surface atoms spontaneously detach from and reattach to surfaces at all temperatures $> 0\text{ K}$, and exert a pressure to the atmosphere surrounding the particle (i.e., the *vapor pressure* if the atmosphere is gaseous). This pressure increases with increasing temperature (i.e., detachment probability increases) and surface-to-volume ratio of the nanoscale object (i.e., the fraction of low-coordinated surface atoms increases). In a two-phase system (solid/gas or liquid/gas), a phase transition occurs, when the pressure exerted by two phases is equal, e.g., water boils in air when its vapor pressure reaches atmospheric pressure. Small particles create a higher pressure than large ones and, consequently, reach an equilibrium with its surrounding medium at lower temperatures, i.e., smaller objects exhibit lower values of T_m , [91] as illustrated in Fig. 4.3.

In Chapter 3, the temperature-dependence of the adatom diffusivity was discussed, and the homologous temperature $T_H = T_s/T_m$ was identified as proxy for adatom mobility, i.e., diffusion is promoted with increasing T_s and/or decreasing T_m . The rearrangement of atoms to accommodate the increasing lattice parameter in growing nano particles is diffusion-dependent, and it is thus facile in small particles with low T_m . Upon increasing particle size, atoms become less mobile, and the lattice parameter cannot further increase, i.e., a smaller-than-equilibrium lattice parameter is locked into the particle, and compressive stress forms. [89] The above-described scenario is illustrated in Fig. 4.3(b) through (d), where the equilibrium lattice constant increases from a_2 to a_3 as the particle size increases (Fig. 4.3(b) and (c)), but due to insufficient mobility, it is locked at the lower value a_2 , and the particle is strained (Fig. 4.3(d)).

The island size at which the lattice parameter is locked into the island (i.e., the critical thickness t_o and the critical diameter d_o) is an essential quantity for determining the magnitude of the compressive stress that builds up during island growth, i.e., the earlier during growth the lattice constant is locked, the larger the induced compressive stress. A model by Cammarata *et al.* [89] predicts the stress σ of a cylindric island (thickness t , diameter d) which is given by

4.2 Stress during island formation and growth

$$\sigma = (f + g) \left(\frac{1}{t} - \frac{1}{t_o} \right) + 2\beta h \left(\frac{1}{d} - \frac{1}{d_o} \right), \quad (4.4)$$

where f and h are the surface stresses of the round surface and curved surface, respectively, g is the film/substrate interface stress, and β is a function of the elastic compliances of the crystallite island. From Eq. 4.4 follows that σ increases with decreasing t_o and d_o (for $\beta > 0$).

Friesen and Thompson [92,93] studied stress evolution during island nucleation and growth, and found that the compressive stress relaxes during deposition interruptions, which they attribute to adatom/surface interactions. High adatom concentrations on the surface may lead to restructuring of surface atoms, which increases the surface stress. During interruptions, the adatom population decreases fast, and surface atoms move to equilibrium positions, i.e., surface stress relaxes.

4.3. Stress during island coalescence—grain boundary zipping

Coalescence is the reshaping of a pair (or cluster) of islands until near-equilibrium shape is reestablished, and it is the dominant island growth mechanism during sputter-deposition of thin films (see Chapter 3 for more details). The initial step of a coalescence process is the impingement of two neighboring islands. This energy-minimization process introduces tensile stress in the coalescing island pair: Just before impingement, two surfaces exist (island/vacuum interfaces), separated by a small gap, as indicated by the surface profile $y(z)$ in Fig. 4.4(a) (where z is the film growth direction).

Impingement leads to the formation of an interface (i.e., grain boundary GB), which has a lower energy than two surfaces. In this process, which can be seen as the inverse of crack formation and propagation, the driving force for energy-minimization is large enough to elastically deform the island lattice to form the interface, i.e., tensile stress is introduced into the coalescing island-pair. Once the first planes are zipped together, the gap between islands closes from bottom (substrate) to top, and it only stops when the energy needed for elastic straining of the crystal lattice becomes too large (note that the gap size increases with distance from substrate). The resulting reshaping of the surface profile, and generation of stress profile $\sigma(z)$, predicted by Nix and Clemens [94], are indicated in Fig. 4.4(b).

Fig. 4.4: (a) Surface profile $y(z)$ before coalescence, and (b) elastic displacement of $y(z)$ and stress profile $\sigma(z)$ accompanied by the coalescence of isolated crystallites. Grain boundaries (GB) are indicated after coalescence. Reprinted with permission from Ref. [94].

Seel *et al.* [95] observed that the Nix-Clemens model overestimates the tensile stress generation during coalescence, and found that the stress generated by island impingement and GB zipping is strongly dependent on the boundary conditions at the island/substrate interface. In their model, they investigate the effect of islands that are perfectly bound at the interface (i.e., *traction* in Fig. 4.5(a)) vs. islands that can accommodate strain by *sliding* at the interface. Furthermore, they compare the first impingement of an island (cases (i) and (iii) in Fig. 4.5(a)) to the impingement on an island that is part of a coalescing island pair (cases (ii) and (iv) in Fig. 4.5(a)). The resulting stresses as function of island radius are presented in Fig. 4.5(b). Smaller stress forms with increasing island radius, independent of the boundary conditions, however, while tensile stress is formed in an island that is bound firmly to the substrate (island (i)), the center of mass of an island that slides at the interface moves toward the GB (island (iii)), inhibiting tensile stress formation.

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Furthermore, if perfect sliding occurs, no stress is transmitted to the substrate, and no stress generation can be measured via techniques that monitor the film stress-induced change of substrate curvature (see Section 5.2.2). This mechanism is a potential reason for the overestimation of the tensile stress formation with the Nix-Clemens model.

Fig. 4.5: (a) Surface profiles of islands before (dashed lines) and after (solid lines) impingement of (i) one and (ii) two islands with perfect traction at the island/substrate interface, and impingement of (iii) one and (iv) two islands that can freely slide at the island/substrate interface. (b) Evolution of stress due to island impingement and grain boundary zipping vs. island radius for plane strain conditions for islands illustrated in (a). Reprinted with permission from Ref. [95].

Zhou *et al.* [96] investigated stress generation during island coalescence with molecular dynamics simulations, and found that the stress magnitude is strongly influenced by the shape of coalescing islands. In their simulations, atoms are deposited onto a pre-structured substrate with islands, which are separated by a gap that is too large for GB zipping to occur without deposition. In Fig. 4.6(a), the in-plane stress evolution with time during deposition of Fe onto two Fe islands is presented. For square island shapes that have flat and parallel island walls, and consequently a large contact area, tensile stress forms as islands coalesce via GB zipping, and a dense island is formed (see inset #1 in Fig. 4.6(a)). Concurrently, cylindrical and hemispherical islands, which have smaller contact areas than square islands, show no tensile stress formation, which the authors attribute to coalescence via gap filling by arriving Fe atoms, i.e., no GB zipping occurs since island walls are separated by too large gaps.

Simulations of the stress evolution due to coalescence in case of a polycrystalline film are presented in Fig. 4.6(b) for different surface morphologies, [96] where the contact area is decreased/the island gap increased by decreasing the island wall-to-substrate surface angle from 90° (perpendicular edge) to 58° (shallow groove). With decreasing angle, the maximum impingement tensile stress decreases, due to less pronounced GB zipping, e.g., compare maximum tensile stress ~ 3 GPa for perpendicular edge to ~ 2 GPa for deep surface grooves (i.e., angle 75°). For deposition on a flat surface (not shown here), no tensile stress is observed. In reality, island shapes are more complex than those modelled in Ref. [96], e.g., convex surface profiles form between the island center and the substrate (see Figs. 4.4 and 4.5). Simulation of the stress evolution upon coalescence of such islands would result in stress magnitudes ranging between the values for perpendicular island walls and flat surfaces.

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Coalescence is fully completed upon formation of a single-crystal island, which, per-definition, means that the GB and the resulting tensile stress have been eliminated, i.e., no permanent tensile stress is formed. Concurrently, stress from early film formation stages due to the Laplace pressure is annihilated during coalescence, as atoms are rearranged. With increasing island size (R), the coalescence-completion time t_{coal} increases ($t_{coal} \sim R^4$) [41,48], while the average island separation distance decreases, i.e., average time t_{imp} between impingement processes becomes shorter. When $t_{imp} < t_{coal}$, islands start impinging upon coalescing island-pairs, and coalescence cannot be completed. This leads to a net tensile stress in the films, which is a sign of incomplete coalescence.

Fig. 4.6: (a) Simulated stress evolution as function of deposition time for Fe films with #1 square, #2 cylindrical, and #3 hemispherical island shapes. Insets show the island shape after deposition completion. (b) Simulated stress evolution vs. film thickness of W films with #1 perpendicular edge islands (island wall-to-substrate surface angle 90°), #2 deep surface grooves (angle 75°), #3 shallow surface grooves (angle 58°). Insets show surface morphologies of #1 through #3 before deposition. Reprinted with permission from Ref. [96].

4.4. Stress formation and evolution in continuous films

Application-relevant film thicknesses are typically much larger than those at which continuous layers are formed. Hence, it is important to understand stress formation beyond the stage of island coalescence. The discussion of the stress evolution in continuous films is complex, as the effect of several independent and inter-related mechanisms must be considered. Without knowledge of the film microstructural evolution, a discussion is not possible, as properties like grain size and texture, surface roughness, or film density are key to understanding which stress-contributing processes are active/dominant. In this section, studies on stress evolution in continuous films are presented phenomenologically; models that allow calculating stress during film growth are outlined in Section 4.6. Data presented in this section stems from growth of polycrystalline films that show no epitaxial relation to the substrate, i.e., stress formation mechanisms discussed in Section 4.1.2 are not relevant.

4.4.1. *Effect of atomic mobility on stress generation and evolution*

The stress evolution close to and after continuous film formation is strongly dependent on the adatom mobility, [97] i.e., the sign and magnitude of stress in continuous films are not material constants, but functions of deposition parameters and of the resulting film morphological evolution. [98]

Low atomic mobility conditions (i.e., obtained at T_H values below 0.2) may yield average adatom diffusion lengths that are shorter than the lateral grain size, such that adatom-GB interaction is inhibited. [90] In this case, adatoms contribute only to the out-of-plane propagation of the film growth front and the evolution of the surface roughness (columnar growth). At GB triple junctions (i.e., GB-vacuum interface), the GB height increases by elastic snapping of lattice planes, and thus tensile stress forms in the film (as described in Section 4.3). As in this case, the overall mobility of atoms is low (i.e., bulk diffusion is not active), the film microstructure does not evolve during deposition, and no additional stress contributions need to be considered. Consequently, a tensile steady-state is obtained, the magnitude of which is proportional to the GB number density at the surface.

Figure 4.7 presents Fe and Cu films that are grown at conditions of low atomic mobility, i.e., 300 K for Fe on oxidized Si(001) substrates and 110 K for Cu on mica(001). [84,99,100] These temperatures correspond to $T_H = 0.20$ and 0.08, respectively, where diffusion of atoms is expected to be kinetically limited (see Section 3.6.1), and a porous film with columnar grains forms. [50] From the film force evolution vs. film thickness, the onset of island coalescence and tensile stress formation can be seen (i.e., at ~ 2 nm for Fe and ~ 8 nm for Cu), however, no further morphological information can be deducted. We also note that the stress does not evolve after deposition interruption (marked by arrows in Fig. 4.7).

4 Stress generation and evolution during thin film growth

Stress evolutions during deposition at higher temperatures are also presented in Fig. 4.7, i.e., Fe film growth at 520 K ($T_H = 0.34$), and Cu growth at 300 K ($T_H = 0.22$) whereby surface diffusion is active. [3] A characteristic tensile film force maximum is found for both cases (at ~ 10 nm for Fe and ~ 18 nm for Cu); the thickness of this tensile peak has been shown to correspond to the continuous film formation thickness h_{cont} . [101] The tensile stress forming for mean film thickness $h_f < h_{cont}$ corresponds to stress owing to island coalescence, while the compressive stress observed for $h_f > h_{cont}$ is associated with atomic-scale processes occurring in continuous layers. We note that the magnitude of tensile stress for $h_f < h_{cont}$ is identical for low and high mobility conditions (300 K vs. 520 K for Fe and 110 K vs. 300 K for Cu), which indicates that the island nucleation and coalescence stages are similar (i.e., island number densities, island sizes). Further increase of the temperature to 570 K for Cu ($T_H = 0.42$), causes the tensile peak to shift to higher film thickness (~ 40 nm), which indicates that island coalescence is active to higher film thicknesses, due to lower island number density and larger islands resulting from increased surface diffusion at this temperature (and, thus, faster coalescence). [99] Another characteristic feature of the stress evolution in films deposited at high atomic mobility conditions is the tensile stress evolution upon deposition interruption (indicated by arrows in Fig. 4.7), which is revisited in Section 4.5.

Fig. 4.7: Evolution of film force per unit width vs. film thickness for evaporated polycrystalline Fe films on oxidized Si(001) and Cu films on mica(001) for different deposition temperatures. The respective deposition rates are indicated in the figure. Arrows indicate the point at which deposition flux is terminated. Reprinted with permission from Ref. [84].

The most widely accepted theory with regards to the origin of compressive stress during deposition at high atomic mobility conditions suggests that a gradient of the chemical potential develops during film deposition between the surface and GBs, owing to the large difference in adatom number density. [102] This chemical potential difference is the driving force for flux of excess atoms into GBs, where they (i) decrease the tensile straining of the lattice induced via snapping, and (ii) increase the density at GBs, leading to compressive stress formation.

Consequently, the compressive stress formation is proportional to the GB number density, and a compressive steady-state stress (as seen for high atomic mobility conditions in Fig. 4.7) is formed, if the adatom/GB interaction is unchanged, i.e., no changes in GB number density and adatom mobility occur with continued film thickening. A detailed description of this model and other stress-generation mechanisms that are suggested in the literature are given in Section 4.6.

4.4.2. Grain growth and stress

When films are grown at conditions where surface and bulk atomic diffusion are active (i.e., for $T_H > 0.2$ and $T_H > 0.4$, respectively), the film morphology evolves with increasing film thickness. One key morphological feature of thin films is the grain size, the change of which (also referred to as grain growth) is a mechanism that is driven by a minimization of the total film energy. Energy minimization is achieved by elimination of GBs, which increase the interface energy, and by increasing volume fractions of low-energy crystallographic orientations. This growth can be mainly active close to the growth front, leading to V-shaped grains and to a continuous decrease of the GB number density at the film surface (i.e., when surface diffusion is active for $0.2 < T_H < 0.4$). [3] When bulk diffusion is active ($T_H > 0.4$), grain growth occurs throughout the film thickness, resulting in columnar grains with their grain size increasing along the film growth direction.

GBs are regions of low atomic density in thin films, i.e., the elimination of GBs during grain growth is accompanied by tensile stress formation, as the lattice of the growing grain has to accommodate the “missing volume” created when forming dense grains. Figure 4.8 presents film force evolution vs. film thickness during growth of Ni films at temperatures ranging from 300 to 473 K (i.e., $T_H = 0.17$ to 0.27). [98] Initially, the film force evolves following the tensile-compressive evolution discussed in Section 4.4.1 for the high atomic mobility regime, however, with increasing film thickness, no compressive steady-state stress is observed, but a transition to tensile stress formation occurs (indicated by arrows). With increasing substrate temperature, the transition toward the tensile regime is shifted to larger film thicknesses.

Yu and Thompson [98] argued that the stress evolution seen in Fig. 4.8 is the result of the competition among tensile stress formation due to grain growth, and compressive stress formation due to adatom attachment to GBs. Initially, adatoms at the growth front diffuse to GBs and compensate the tensile stress forming due to grain growth, i.e., a net compressive stress forms in the film. With increasing film thickness, the average lateral grain size increases, while the diffusion length of adatoms remains constant, and fewer adatoms reach the GBs, leading to a net tensile stress formation. With increasing substrate temperature, the diffusion length of adatoms increases, and the compressive-to-tensile stress transition is shifted to larger film thicknesses. It is noted that the latter shift is seen in this system because the grain size of the Ni film does not increase with substrate temperature in the investigated temperature range.

4 Stress generation and evolution during thin film growth

Fig. 4.8: Evolution of film force per unit width vs. film thickness for Ni films deposited at temperatures 300 to 473 K; the respective homologous temperatures T_h are indicated in the figure. Films are grown via electron-beam evaporation with deposition rate 0.05 nm/s. Arrows indicate the transition from compressive stress (i.e., negative slope) to tensile stress formation (i.e., positive slope). Reprinted with permission from Ref. [98].

The question whether grain growth leads to a compressive-to-tensile stress transition is not easily answered, as the interplay among adatom diffusion length and lateral grain size determines which stress-state prevails. Comparing Cu growth at 300 K ($T_H = 0.22$, Fig. 4.7), which was introduced as example for the high atomic mobility growth regime, to Ni growth at 373 K ($T_H = 0.22$, Fig. 4.8), shows that knowledge of T_H is not sufficient to predict the stress evolution. Based on the data for Ni presented in Fig. 4.8, it can be expected that tensile stress will always prevail, if thick enough films are deposited, and grain size increases with film thickness. However, the viability of this hypothesis cannot be easily explored, as *in situ* stress studies usually focus on early film growth stages, therefore data for thick films is not readily available.

4.4.3. Stress formation under energetic bombardment

In Sections 4.4.1 and 4.4.2, stress data from films grown via evaporation have been presented. The general trends in stress formation in polycrystalline films discussed so far (high/low mobility, grain growth) are also valid for sputter-deposited films. However, an additional effect needs to be considered: interactions of hyperthermal noble gas and sputtered species with the growing film lead to *atomic peening*, i.e., a linear sputter cascade in the film that leads to film densification. [103] Atoms that are displaced via atomic peening can cause GB densification, which yields biaxial compressive stress in the film, or be implanted in grains, where they lead to a hydrostatic stress. [104–106]

4.4 Stress formation and evolution in continuous films

Figure 4.9(a) presents the evolution of film force vs. film thickness for sputter-deposited Cu films on Si(100) for three working pressures. [84,107] All films show a tensile stress maximum during initial growth stages (see insert in Fig. 4.9(a)), indicating continuous film formation, and compressive stress formation thereafter. For low working pressures (0.05 Pa), the compressive stress exhibits a steady-state in the observed thickness range, while a transition to tensile stress is observed for higher working pressures (0.5 and 2 Pa). After deposition interruption, stress changes are observed for all cases, indicating a high atomic mobility. Pletea *et al.* [107] found that the tensile stress evolution at high working pressure stems from a porous microstructure of Cu films with large surface roughness, while films are dense when compressive stress is observed. At low working pressure, film forming species experience few collisions while in the vapor phase and have a wide range of energies. Atoms that arrive with high kinetic energy can initiate sputtering of the film and promote atomic mobility by momentum transfer. With increasing working pressure, interatomic collisions in the vapor phase become more frequent, and the average energy distribution of vapor atoms is shifted to lower energies, i.e., film densification by collision-induced displacement is less common, and porous films form. [108]

Fig. 4.9: Evolution of film force per unit width vs. film thickness for (a) sputter-deposited polycrystalline Cu films on Si(100) substrates for various working pressures, and (b) evaporated polycrystalline Cu films on MgF₂/glass substrates for various oxygen partial pressures. The inset in (a) shows the film force evolution during early growth stages. Essential deposition parameters (substrate temperature, deposition rate, base pressure in (b)) are indicated in the figures. Arrows indicate the point at which deposition flux is terminated. Reprinted with permission from Ref. [84].

Atomic peening has been studied more closely at low atomic mobility conditions (Mo and Ta, sputter-deposited at 300 K, i.e., $T_H = 0.10$ and 0.09, respectively). [109–111] While tensile stress forms in these films at conditions where no bombardment with energetic particle occurs (e.g., in evaporation), compressive stress with increasing magnitude has been observed in sputter-deposited films with (i) decreasing working pressure, (ii) increasing bias potential,

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and (iii) increasing deposition rate. This is understood in light of generation of point defects in the crystal lattice by collision-induced atom displacements when pressure is decreased and/or substrate bias potential is increased. Concurrently, defect annihilation by diffusion to the growth front is inhibited with increasing deposition rate. [106]

4.4.4. *Effect of impurities on stress formation*

Impurities can promote or inhibit fundamental structure-forming processes, and thus determine the film microstructural evolution during growth (see Section 3.6.4). [3] Consequently, the presence of impurities during film growth impacts the formation of intrinsic stress. Deposition of thin films in ultra-high vacuum (UHV) chambers (i.e., base pressure $< 10^{-5} Pa$) ensures that contamination of the growing film and impurity incorporation from the chamber background are minimized. During growth in high vacuum (HV) chambers, incorporation of oxygen-containing species might alter the film morphology and stress-state.

Abermann and Koch [112] investigated the effect of oxygen on the stress evolution in evaporated Cu films by introducing oxygen gas into an UHV chamber, to verify measurements performed in a HV chamber. [113] Figure 4.9(b) presents the evolution of film force with film thickness of Cu films deposited in various oxygen containing atmospheres. [84,112] For the lowest oxygen pressure ($< 1 \times 10^{-8} Pa$), a tensile-compressive stress evolution is found with a compressive steady-state in the continuous film regime. With increasing oxygen pressure, the tensile stress maximum is shifted to lower thicknesses, and a larger compressive stress is observed after continuous-layer formation. However, this compressive stress is not in a steady-state, and a transition to tensile stress is found; the thickness of the compressive-to-tensile stress transition decreases with increasing oxygen pressure. After deposition interruption (indicated by arrows in Fig. 4.9(b)), stress continuous to evolve for all deposition conditions.

The addition of oxygen in the atmosphere leads to the formation of copper-oxide nano particles at the film growth front, which stabilize smaller Cu islands during nucleation, thus leading to a decrease of the continuous film formation thickness (i.e., the tensile peak in Fig. 4.9(b)). [112] Presence of nano particles in the Cu matrix hinders GB migration (i.e., *solute drag*), [53] consequently, lateral grain growth is stopped during film deposition. The higher GB number density of films deposited in oxygen-containing atmospheres leads to increased compressive stress. Additionally, Cu adatom mobility is decreased due to the copper-oxygen interaction, and a porous columnar grain structure forms, leading to tensile stress formation.

4.5. Stress evolution after deposition interruption

During the discussion of stress data in Section 4.4, the stress evolution after deposition interruption has been mentioned several times. In Fig. 4.7, tensile stress formation is observed after deposition interruption for Cu and Fe film evaporation at high atomic mobility conditions (i.e., 300/570 K and 520 K, respectively), while no stress evolution is observed for low mobility conditions (i.e., 110 K and 300 K, respectively). During interruption of sputter-deposition of Cu films (see Fig. 4.9(a)), tensile stress formation is found for low working pressure (0.05 and 0.5 Pa), while compressive stress forms after deposition of porous Cu films at high working pressure (2 Pa). Evaporation of Cu films in various oxygen-containing atmospheres (see Fig. 4.9(b)) leads to films that show a tensile stress behavior after deposition interruption below an oxygen pressure 2.7×10^{-5} Pa, and compressive stress at an oxygen pressure 1.3×10^{-4} Pa.

These results show that process parameters strongly affect the stress evolution after deposition interruption. In general, a stress evolution is observed for high mobility deposition conditions (i.e., high T_H). The fact that film stress during and after deposition are not the same underscores the necessity for *in situ* stress analysis since *ex situ* stress analyses cannot capture film stress variations upon deposition interruption. In addition, thermal stress must be considered when analyzing stress evolution, for the reasons explained in Section 4.1.1.

A systematic investigation of the stress evolution in the high atomic mobility regime after deposition interruption has been performed by Flötto et al. [114]. Figure 4.10(a) presents the evolution of the film force per unit width vs. time after deposition interruption for evaporated Ag films with grain sizes in the range 63 to 436 nm. The magnitude of the tensile stress increases with decreasing grain size, which indicates that the GB number density is related to the post-deposition stress evolution. This is further strengthened by the lack of stress formation after deposition interruption in an epitaxial Ag film, which is single-crystalline, and therefore free of GBs. Furthermore, the authors show that the post-deposition tensile stress rise is linearly proportional to the inverse of the grain size (see Fig. 4.10(b)), while changes in the deposition rate and film thickness do not significantly influence the stress magnitude if the grain size remains constant.

Concurrently, increasing grain size and deposition rate lead to faster development of the post-deposition tensile stress rise. This can be seen in Fig. 4.10(a), where the stress evolution has stopped after 900 s for grain size 436 nm, while a tendency for further tensile stress formation is observed for films with smaller grain sizes.

4 Stress generation and evolution during thin film growth

Fig. 4.10: (a) Evolution of the film force per unit width vs. time after growth interruption for evaporated Ag films on SiO_2 at 300 K with lateral grain sizes in the range 63 to 436 nm, and an epitaxial Ag film on $\text{Si}(100)$ (epitaxial relation $\text{Ag}(100) \parallel \text{Si}(100)$ and $\text{Ag}[1\bar{1}0] \parallel \text{Si}[1\bar{1}0]$). Data is shifted to zero film force for convenience. (b) Dependence of the film force per unit width after 900 s growth interruption (see final value in (a)) on the inverse lateral grain size for various deposition rates (colors) and film thicknesses (symbols). Reprinted with permission from Ref. [114].

Another aspect of the stress evolution upon deposition interruption is its reversibility if film growth is resumed. Figure 4.11 presents *in situ* stress data obtained during the evaporation of Au films, [115] which show a typical compressive-tensile-compressive stress evolution with increasing film thickness with a compressive steady-state, characteristic for the high atomic mobility regime. When film deposition is interrupted, a tensile rise is observed. The growth interruption is indicated by blue arrows in Fig. 4.11, while the stress evolution with time after deposition interruption is not presented here (see Ref. [115] for data). If film growth is resumed after 5 min growth interruption (Fig. 4.11(a)), initially, very strong compressive stress is formed in the film (see large negative slope), which decreases within deposition of few nanometers of film until the stress magnitude of the compressive steady-state is reached (the film recovers the same stress value prior to interruption, indicated by red dashed line). This reversible stress evolution is reproducible, as seen for the three consecutive growth interruptions presented in Fig. 4.11(a). In a second set of depositions, presented in Fig. 4.11(b), growth interruptions are much longer (i.e., 24 h). While the general stress evolution with growth interruption is the same as for short growth interruptions, the post-interruption stress does not reach the compressive stress magnitude before interruption, but remains shifted to a less compressive/more tensile level (indicated by red arrow in Fig. 4.11(b)).

Yu *et al.* [115] found that the stress data during growth interruption is best fitted with an exponential decay function with two time constants ($\tau_1 \cong 10^2$ s, $\tau_2 \cong 10^4$ s). The fast process dominates the stress evolution during short growth interruptions and is reversible. Its time scale is comparable to surface diffusion-dependent changes of the surface morphology. [116,117] The slow process is irreversible and active in much longer time scales, indicating that its underlying process is a bulk effect, e.g., grain growth and recrystallisation that are active during growth interruptions.

4.5 Stress evolution after deposition interruption

Fig. 4.11: Evolution of the film force vs. mean film thickness during evaporation of Au films on $\text{Si}_3\text{N}_4/\text{Si}(100)$ at 300 K with deposition rate 0.05 nm/s. Blue arrows mark (a) 5 min and (b) 24 h deposition interruptions, during which a tensile stress evolution is observed. While the pre-interruption stress evolution is retained in (a), a tensile shift occurs in (b). Reprinted with permission from Ref. [115].

4.6. Models for stress formation and evolution in continuous films

Stress generation processes in discontinuous films (see Sections 4.2 and 4.3) are well understood and accepted within the research community. In contrast, no consensus exists with regards to mechanisms that govern stress in continuous layers. The literature survey presented in Sections 4.4 and 4.5 show common features that allows for drawing the following conclusions:

- (i) Tensile stress prevails in continuous films deposited at low atomic mobility conditions.
- (ii) Compressive stress forms in continuous films if atomic mobility is high.
- (iii) The magnitude of stress in thin films is correlated with the GB number density.
- (iv) Decrease of the GB number density (i.e., grain growth) during or after film growth, yields tensile stress.
- (v) Porous microstructures are associated with tensile stress.
- (vi) During growth interruptions at high atomic mobility conditions, a tensile stress evolution is observed that is reversible when deposition is resumed.

Based on the afore-mentioned conclusions and correlations, several mechanisms and models have been proposed in the literature that allow for calculating and predicting intrinsic stress σ_i during thin film growth as function of deposition parameters (e.g., substrate temperature, vapor arrival rate), morphological features (e.g., grain size), and material constants (e.g., lattice parameter, melting temperature). The following sections outline such models.

4.6.1. Adatom/grain boundary interaction

A kinetic model based on rate equations was developed by Chason *et al.* over the last two decades. [15,102,118–120] It is based on diffusion of adatoms from the film surface into GBs during film deposition. This diffusion is driven by differences of the chemical potential of adatoms at the film surface μ_S and within GBs μ_{GB} . During deposition, the vapor arrival rate leads to an increase of μ_S from the equilibrium value μ_S^0 to $\mu_S^0 + \delta\mu_S$. The chemical potential of adatoms in a GB is initially μ_{GB}^0 and changes to $\mu_{GB} = \mu_{GB}^0 - \sigma\Omega$ during deposition, i.e., it increases if compressive stress ($\sigma < 0$) forms in the film; Ω is the atomic volume of the film-forming species. At equilibrium, $\mu_S^0 \cong \mu_{GB}^0$, [118] and the difference in chemical potential $\Delta\mu$ during deposition is

$$\Delta\mu = \mu_S - \mu_{GB} \cong \delta\mu_S + \sigma\Omega = (\sigma - \sigma_{comp})\Omega, \quad (4.5)$$

where $\sigma_{comp} = -\delta\mu_S/\Omega$. A driving force for adatom insertion into the GB exists if $\Delta\mu$ is positive, while adatoms in the GB diffuse toward the surface for $\Delta\mu < 0$ (see Fig. 4.12(a) for a schematic illustration).

4.6 Models for stress formation and evolution in continuous films

Fig. 4.12: (a) Schematic representation of the stress formation model based on adatom insertion into grain boundaries (GB). Equilibrium chemical potentials of adatoms at the surface and in GBs are μ_s^0 and μ_{GB}^0 , respectively. The flux of atoms to the surface during deposition increases the surface chemical potential by $\delta\mu_s$, and stress σ changes the GB chemical potential by $\sigma\Omega$, where Ω is the atomic volume. (b) Evolution of stress-film thickness product vs. mean film thickness during electron-beam evaporation of Ni films at substrate temperatures 300 to 473 K with deposition rate 0.05 nm/s. Colored lines represents experimental data (see Ref. [98]) and black lines are stress predicted by the stress model on basis of adatom insertion into GBs. Reprinted with permission from Ref. [15].

The change of the stress-film thickness product due to adatom insertion into the GB $(\sigma \times h_f)_{insert}$ as function of time t can be written as

$$\frac{d(\sigma \times h_f)_{insert}}{dt} = -\frac{Y_f \Omega^{2/3}}{L} \frac{dN}{dt}, \quad (4.6)$$

where Y_f is the film biaxial modulus, L is the lateral grain size, and N is the number of adatoms inserted into the GBs. The rate of adatom insertion into GBs, dN/dt , is given by

$$\frac{dN}{dt} \cong 4C_s \frac{D}{\Omega^{2/3}} \frac{\Delta\mu}{k_B T}, \quad (4.7)$$

where C_s is the concentration of mobile species on the surface, D is the effective diffusivity for adatom migration from the surface to the GB, k_B is the Boltzmann constant, and T is the absolute temperature. Combining Eqs. 4.5 through 4.7 gives

$$\frac{d(\sigma \times h_f)_{insert}}{dt} = -\frac{4C_s Y_f \Omega D}{k_B T} \frac{1}{L} (\sigma - \sigma_{comp}) = -\frac{\beta D}{L} (\sigma - \sigma_{comp}). \quad (4.8)$$

The second mechanism that is considered in the model by Chason *et al.* is the stress that forms due to GB zipping at the growth front (see Section 4.3), which progresses with the same speed as the deposition rate F . Tensile stress σ_{tens} forming due to the elastic formation of the crystal lattice is proportional to $(\Delta\gamma/L)^{1/2}$, where $\Delta\gamma$ is the change of interfacial energy when a GB is formed at the cost of two film/vacuum interfaces. [94,118,121] The time derivative of the stress-thickness product change due to GB zipping $(\sigma \times h_f)_{zip}$ reads

$$\frac{d(\sigma \times h_f)_{zip}}{dt} = F \sigma_{tens}(L). \quad (4.9)$$

4 Stress generation and evolution during thin film growth

Grain growth removes GBs and leads to tensile stress formation in the bulk of the film. If $L(z)$ is the grain size during the deposition of a layer at film thickness z , and $L(h_f)$ the grain size at the final film thickness h_f , the growth of the film from z to h_f has removed $1/L(z) - 1/L(h_f)$ GBs per unit length in the layer deposited at thickness z . If Δd is the excess volume per unit area that is removed during grain growth, the stress-thickness product due to grain growth $(\sigma \times h_f)_{gg}$ is

$$(\sigma \times h_f)_{gg} = Y_f \Delta d \int_0^{h_f} \left(\frac{1}{L(z)} - \frac{1}{L(h_f)} \right) dz. \quad (4.10)$$

Integration over the film thickness and calculation of the time derivative of Eq. 4.10 gives

$$\frac{d(\sigma \times h_f)_{gg}}{dt} = Y_f \Delta d h_f \left(\frac{1}{L(h_f)^2} \frac{\partial L(h_f)}{\partial t} \right). \quad (4.11)$$

Since grain size increases with time (i.e., $\partial L(h_f)/\partial t > 0$), this stress contribution will always lead to a tensile stress component. The summation of Eqs. 4.6, 4.9 and 4.11 gives the overall stress-thickness product evolution with time

$$\frac{d(\sigma \times h_f)}{dt} = F \sigma_{tens}(L) - \frac{\beta D}{L} (\sigma - \sigma_{comp}) + Y_f \Delta d h_f \left(\frac{1}{L(h_f)^2} \frac{\partial L(h_f)}{\partial t} \right). \quad (4.12)$$

Since stress data is usually presented as function of film thickness, the variable transformation $dh_f = F dt$ gives

$$\frac{d(\sigma \times h_f)}{dh_f} = \sigma_{tens}(L) - \frac{\beta D}{FL} \left(\frac{(\sigma \times h_f)}{h_f} - \sigma_{comp} \right) + Y_f \Delta d h_f \left(\frac{1}{L(h_f)^2} \frac{\partial L(h_f)}{\partial h_f} \right). \quad (4.13)$$

With this model, Chason *et al.* [15] were able to fit the stress evolution of Ni for various substrate temperatures, [98] where grain growth was found to be active and responsible for a compressive-to-tensile stress transition (see discussion of Fig. 4.8). The fitting of this data is presented in Fig. 4.12(b), and the authors found that fitting parameters (σ_{tens} , σ_{comp} , βD , $Y_f \Delta d$), which were obtained via non-linear least square fitting of the model to the experimental data, are physical, and reasonably close to reported values (for βD and $Y_f \Delta d$). We note that the fitting range is set to begin past continuous film formation, as stress generation and evolution in continuous films is the main focus.

In cases where the grain size does not increase with increasing film thickness, $\partial L(h_f)/\partial h_f = 0$, and Eqs. 4.12 and 4.13 can be simplified. In this case, a steady-state stress σ_{ss} forms in the film which is [118]

4.6 Models for stress formation and evolution in continuous films

$$\sigma_{ss} = \frac{\sigma_{tens} + \frac{\beta D}{FL} \sigma_{comp}}{1 + \frac{\beta D}{FL}}. \quad (4.14)$$

This version of the stress model can be used to describe high mobility growth, e.g., during Cu growth at 300 K (see Fig. 4.7), where a steady-state stress is found after continuous film formation. Equation 4.14 also captures the transition of a compressive σ_{ss} to tensile σ_{ss} for decreasing substrate temperature and increasing deposition rate. [119]

When the deposition flux is turned off during growth interruptions, the supersaturation of adatoms on the film surface decreases fast, and $\delta\mu_s$ becomes zero (i.e., $\sigma_{comp} = 0$). If σ_{ss} is the stress before growth interruption, a stress evolution

$$\sigma(t) = \sigma_{ss} \exp\left(-\frac{\beta D}{h_f L} t\right) \quad (4.15)$$

is seen with time t thereafter. This stress evolution is in agreement with experiments (see Fig. 4.7, Fig. 4.9, Fig. 4.10), and captures some of the observed features, e.g., a faster tensile rise can be expected for increasing grain size (Fig. 4.10).

The model outlined above is only valid if atom mobility in GBs is high, i.e., the stress within the GB is constant throughout the film thickness. If this is not the case, stress gradients would have to be considered, leading to a more complex description.

An alternative description of the adatom/GB interaction model was presented by Yu and Thompson, [98] to better understand the observed stress regimes (compressive steady-state vs. compressive-to-tensile stress transition in continuous films). Again, stress that forms in the surface layer is distinguished from stress in the bulk of the film (e.g., due to grain growth). In their model, Yu and Thompson argue that the observed stress in continuous films is the result of a competition among adatom attachment to two-dimensional (2D) islands that form on grains and to the GB, where they lead to compressive stress. At low film thicknesses, the grain size L is relatively small, and, on average, only one island forms on top of each grain, because the entire island is the part of the GB capture zone (i.e., the area from which inserted adatoms come). Consequently, the number of adatoms that are inserted into the GB is high, but independent of L . When the grain size increases with film thickness, the grains become larger than the GB capture zones, and the number of adatoms that are inserted into the GB depends on the ratio of average island spacing to grain size, i.e., less adatoms are inserted with increasing grain size.

With this model, Yu and Thompson explain the stress evolution in Ni films (see Fig. 4.8) as follows: [98] Shortly after continuous film formation, the island size is small, and the compressive stress component due to adatom attachment to GBs is large, while tensile stress due to grain growth (similar to Eq. 4.11) is small, i.e., compressive stress forms in all films. With increasing grain size, the compressive

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stress component becomes smaller, while the tensile stress component increases, i.e., a compressive-to-tensile stress transition is seen when these two components are equivalent. Increasing substrate temperature leads to an increase of the adatom diffusion length, which increases the compressive stress component, and shifts the stress transition to larger film thicknesses.

The models described in this section are able to reproduce many stress features during and after film growth. Flötotto *et al.* [114] remark that several of the post-deposition stress features that are predicted by the models cannot be verified by experiments (e.g., increasing post-deposition stress rise magnitude and faster kinetics with increasing pre-interruption stress magnitude). Moreover, the models have been criticized because unphysically high GB-to-surface diffusion ratios have to be assumed in simulations to match compressive stress magnitudes observed experimentally. [122]

4.6.2. Grain boundary grooving

The fast character of stress evolution during growth interruptions, and the weak film-thickness-dependency of the stress rise indicate that surface processes are responsible for the stress evolution in high atomic mobility systems. Yu *et al.* [117] found in atomic force microscopic (AFM) surface studies that films show deep surface grooves long after deposition has been completed, while these grooves are not observed immediately after deposition. Grooving of surfaces at GB/surface intersections with a dihedral angle that is determined by the surface and interface free energies is described by Mullins. [116] During film growth from the vapor phase, the arriving vapor flux enables diffusion processes at the surface which are not active under equilibrium conditions, e.g., GB zipping leads to GB grooves that are flatter than in equilibrium, and the supersaturation of surface adatoms increases their chemical potential at the surface. Once film deposition is stopped, GB grooves will develop a shape that is closer to the equilibrium shape, i.e., grooves deepen when growth is interrupted. This is illustrated in Fig. 4.13(a).

Figures 4.13(b) and (c) show cross-sectional transmission electron microscopy images of evaporated Ni films, which were deposited at elevated temperature (473 K), where Ni grows in the high-mobility stress regime (see Fig. 4.8), and then cooled to 300 K, where diffusivity is much slower and surface profile reshaping not expected (see Ref. [117] for more experimental details). For immediate cooling after deposition (Fig. 4.13(b)), GB grooves are very flat, while deep grooves are seen for cooling 60 min after deposition interruption (Fig. 4.13(c)). The redistribution of atoms necessary for this reshaping is a surface diffusion process along GBs. For deepening of the GB groove by Δh , the stress-thickness product change is proportional to $\sigma^* \Delta h$, where σ^* is the compressive stress in the surface layers of the film due to trapped adatoms. When growth is resumed, the GB grooves become shallow again with a high number density of trapped atoms near the surface, leading to the apparent reversibility of the stress evolution during growth interruptions.

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Fig. 4.13: (a) Schematic illustration of grain boundary grooves during (dotted line) and after (full line) deposition, where the dihedral angle steepens. Cross sectional transmission electron microscopy images of electron-beam evaporated Ni films (deposition rate 0.5 nm/s) (b) 0 min and (c) 60 min after growth interruption. Shallow grain boundary grooves can be seen in (b), while deep grooves are seen in (c). The scale bar is 10 nm. Reprinted with permission from Ref. [117].

GB grooving is able to explain the post-deposition stress evolution observed by Flötotto *et al.* [114]. The post-deposition tensile rise magnitude depends on the stress before deposition interruption (σ^*) and Δh , i.e., even when σ^* increases, less post-deposition tensile stress can be formed, if Δh decreases. More shallow GB grooves can be expected to form with increasing deposition rate due to larger adatom flux to GBs and faster growth front progression. The kinetics of the stress evolution during growth interruptions depends on the kinetics of the GB groove deepening, which is proportional to $t^{1/4}$. [116]

Vasco and Polop [123] note that GBs observed with AFM do not correspond to the space between individual grains, but rather to bundles of grains that are separated by pseudo-coherent GBs. Other surface (e.g., scanning tunnel microscopy) or crystallographic techniques (e.g., selected area electron diffraction) are able to resolve these bundles. The GB grooving model outlined above does not distinguish between different types of GBs. Furthermore, Vasco and Polop argue that equilibrium GB profiles cannot be modified easily, unless certain regions grow preferentially (e.g., due to shadowing).

Advanced AFM techniques such as force modulation microscopy (FMM) [117] allow the mapping of the residual stress of the film surface, [118] and can therefore give valuable information on the local stress distribution. Vasco *et al.* have developed a stress model based on surface studies of polycrystalline Au films using FMM. [126,127] A residual stress map and corresponding surface topography and stress profiles are presented in Fig. 4.14(a) and (b), respectively. GB grooving is visible in the topographic profile in Fig. 4.14(b) (black line). Their experiments reveal that stress is concentrated close to GBs, with distinct compressive and tensile regions when approaching a GB from the grain center (see red lines in Fig. 4.14(b)). In Fig. 4.14(c) the evolution of calculated surface profiles during film growth (i.e., as a function of deposition time t) is presented; for easier comparison, the profiles are normalized to the GB groove depth h_{GB} .

4 Stress generation and evolution during thin film growth

Equilibrium surface profiles $h_e(r)$ before ($t = 0$ s) and after deposition ($t = 10^4$ s) are present as black and red lines, respectively. Close to the GB, an equilibrium slope m_0 forms due to GB grooving [116], while no surface slope is seen far from the GB. Between these boundaries, $h_e(r)$ follows [116]

$$h_e(r) = 1.77 h_{GB} \operatorname{ierfc}\left(\frac{m_0 r}{1.77 h_{GB}}\right), \quad (4.16)$$

where $\operatorname{ierfc}(x)$ is the integral of the error function of x .

During deposition, an adatom flux toward the GB exists, such that the GB groove approaches asymptotically a flat shape ($m_0 \rightarrow 0$). Since the slope of the surface profile at the GB is constrained, [123] the filling of the GB groove is slow compared to equilibrium conditions (compare GB groove depth of equilibrium (red) and steady-state (green) surface profile in Fig. 4.14(c)). Atoms that cannot diffuse into the GB groove accumulate close to the GB and form a ridge that increases in height with increasing deposition time (blue, teal and green lines in Fig. 4.14(c)). The resulting surface profile corresponds to Mullin's diffusive surface profile. [116]

From the surface profile $h(r)$, the surface curvature $\kappa(r)$ is calculated as

$$\kappa(r) = -\frac{\nabla^2 h(r)}{(1 + [\nabla h(r)]^2)^{3/2}}. \quad (4.17)$$

Equation 4.17 reduces to $\kappa(r) \approx -\nabla^2 h(r)$ for $\nabla h(r) \ll 1$. Where the curvature of the equilibrium surface profile $\kappa_{eq}(r, t)$ differs from the curvature of the diffusive surface profile $\kappa_d(r, t)$, a Laplace pressure

$$\sigma_N(r, t) = 2\gamma_S [\kappa_{eq}(r, t) - \kappa_d(r, t)] \quad (4.18)$$

forms, where γ_S is the surface free energy, and the index N indicates that the intrinsic stress is normal to the surface. The intrinsic stress profiles $\sigma_N(r, t)/2\gamma_S$ resulting from surface profiles presented in Fig. 4.14(c) are drawn in Fig. 4.14(d) and show a tensile stress maximum and a compressive minimum, which is dominant (i.e., compressive stress would be measured when measuring the average stress in the film). The arrows in Fig. 4.14(d) indicate that the stress maxima and minima increase in size and move toward the GB with increasing deposition time. Formation of surface stress in the ridges gives rise to a driving force for ridge-decay to minimize strain energy. [37] This driving force leads to diffusion of surface atoms from the strained GB toward the center of the grain, and thus to the stabilization of a steady-state surface profile.

When deposition it stopped, the driving force for adatom diffusion toward the GB disappears, and the ridge starts to decay driven by strain energy minimization. [37] When the driving force becomes smaller than the energy barrier for surface diffusion, the decay stops. While this decay leads to a decrease of the stress profile (not shown here, see Ref. [127] for details), parts of it persist and correspond to the stress profile measured in Fig. 4.14(b).

4.6 Models for stress formation and evolution in continuous films

Fig. 4.14: (a) Residual stress map obtained from force modulation microscopy on the surface of evaporated Au/Si(111) films. (b) Topography (black line), residual stress (blue line), and discrete stress level (i.e., zero stress, tension, compression, red line) profiles along a grain boundary (GB); location is indicated in (a). (c) Evolution of normalized surface profile $h(r,t)/h_{GB}$, and (d) corresponding intrinsic stress profiles σ_N/γ_s vs. distance r from GB and time t (indicated by colors). m and m_0 are the slopes of the surface profile far from the GB and at the GB, respectively. Arrows in (c) indicate the mass flow, and show the position of the stress maxima in (d). Reprinted with permission from Ref. [127].

With this stress model, stress generation and evolution during film growth can be described: (i) A steady-state surface profile develops during film deposition, which leads to compressive and tensile stress regions close to GBs. As the compressive stress is larger than the tensile stress, compressive stress is measured in the film, when stress is analyzed in average. (ii) Stress relaxation is seen when the deposition flux is stopped. (iii) Kinetics of surface diffusion driven by Mullins-type groove and ridge formation, and strain energy minimization lead to a time constant in the 10^2 s range, which corresponds to experimentally observed values. This model only describes stress formation in the surface layer of a film and does not include bulk effects (e.g., grain growth), i.e., it cannot describe stress evolution in systems where grain growth is active. Additionally, GB/GB interactions are not considered at this stage, which might play an important role to explain effects of deposition temperature and flux. [127]

4 Stress generation and evolution during thin film growth

5. Thin film synthesis equipment and characterization techniques

The present chapter outlines the synthesis equipment and thin film characterization techniques (along with representative measurement data, when relevant) used in the thesis. For detailed experimental setup and measurement details, the reader is referred to appended papers. Section 5.1 describes deposition chambers used to grow thin films and analyze their growth *in situ* and in real-time. Section 5.2 presents *in situ* and real-time techniques to characterize optical, mechanical, and electric properties of films, as well as to determine the composition of the synthesis atmosphere in the chamber. *Ex situ* techniques are presented in Section 5.3, and include methods in which films are probed with electrons and x-rays, as well as real-space surface imaging.

5.1. Deposition chambers

Films were deposited in two magnetron sputter-deposition chambers, a high-vacuum (HV) chamber at the University of Poitiers (base pressure $\sim 8 \times 10^{-6}$ Pa), and an ultra-high-vacuum (UHV) chamber at Linköping University (base pressure $< 10^{-8}$ Pa).

The basic layout of the UHV chamber is presented in Fig. 5.1, but it is conceptually representative for both chambers. The deposition system consists of a main chamber (MC), and load-lock (LL) chamber used for loading samples. The LL chamber features a cassette with five samples positions with a lateral transfer arm for moving samples to the MC. The two compartments are connected through the LL-MC gate valve and separately pumped through their respective turbomolecular pumps (TMP), which are backed with (oil-free) scroll pumps.

The MC TMP is connected to the MC via a throttle valve (TV) that remains fully open when no deposition is running. Working gas (Ar, N₂, O₂) can be introduced i) through the MC wall, ii) close to the three targets, and/or iii) through a gas ring close to the substrate. The working pressure is then set by partially closing the TV, regulated by a loop between the TV motor and the MC Baratron (i.e., capacitance manometer). Pressures are measured with multiple additional pressure gauges (PG): i) MC cold ion gauge, ii) MC Pirani PG (when ion gauge is off), iii) LL and MC are equipped with full range PG, which are combined Bayard-Alpert Pirani gauges, and iv) foreline pressures are measured with Pirani PG.

5 Thin film synthesis equipment and characterization techniques

Fig. 5.1: Schematic illustration of the ultra-high-vacuum system used for thin film deposition in course of the present thesis.

For achieving pressures of $\sim 10^{-8}$ Pa or below in the MC, a bake-out procedure is implemented every time that the entire deposition system is pumped down after exposure to the atmosphere. Bake-out occurs in a specific zone (marked with dashed lines in Fig. 5.1) by heating the chamber to ~ 420 K for ~ 48 h.

The main difference of the HV chamber compared to the UHV system is that a cryogenic pump sustains the vacuum in the MC that is backed by Roots pumps. UHV cannot be reached in this system, as it is not bakeable, i.e., non-metallic gaskets are used.

Film synthesis and *in situ* analysis are performed in the respective MCs of the two systems, which host three magnetron sources for circular targets that are water cooled, and substrate holders that are rotatable and can apply heating to the substrate (see schematic illustration in Fig. 5.2). For ignition of a plasma, working gas is added close to the targets. The MCs are equipped with several shutters that inhibit unwanted deposition of films on the substrate (substrate shutter), unused targets (target shutter), and view ports. Fused silica view ports allow observation of the film growth, e.g., for *in situ* analysis. Two of the *in situ* methods that are employed for growth analysis, i.e., spectroscopic ellipsometry and substrate curvature measurements, are schematically illustrated in Fig. 5.2, i.e., the substrate curvature technique (normal incidence), and spectroscopic ellipsometry (70° angle of incidence with respect to substrate normal). *In situ* substrate curvature and four-point-probe measurements are performed in the HV chamber, while *in situ* spectroscopic ellipsometry is performed in the UHV chamber. More details about these techniques are given in Section 5.2. Thin films deposited for Papers I, II and VI are synthesized in the HV chamber, while Papers III through V are based on films grown in the UHV chamber.

5.1 Deposition chambers

Fig. 5.2: Schematic illustration of the main chamber of a magnetron sputter-deposition system, equipped with in situ measurement techniques that allow analysis of film growth.

5.2. *In situ* characterization

For studying processes that govern film formation and stress evolution, *in situ* and real-time characterization techniques are used, i.e., properties of the film and substrate are monitored during deposition. This approach allows investigations without the sample being affected by atmospheric exposure (which causes, e.g., contamination, oxidation, surface restructuring, relaxation), and provides real-time information, such that kinetics of structure-forming processes can be studied.

5.2.1. *Spectroscopic ellipsometry*

In spectroscopic ellipsometry, the change of the polarization state of light after interaction with a sample surface is used to measure the real and imaginary part of the dielectric function of the probed material as function of incident light frequency. By modelling the dielectric function, information about electronic (e.g., electron number density) and microstructural (e.g., film thickness, surface roughness) properties of the sample can be obtained. Ellipsometry is a surface-sensitive technique, and is used in reflection-mode within this work, i.e., incident polarized light is reflected off the sample under investigation (see schematic setup of light source, polarizer and analyzer in Fig. 5.2).

In the presence of an electric field $\vec{E}$, bound charges (e.g., atomic nuclei, electrons) are displaced. This process is described by the electric displacement field $\vec{D} = \epsilon_0 \vec{E} + \vec{P}$, [128,129] where ϵ_0 is the vacuum permittivity, and $\vec{P}$ is the polarization. For homogeneous isotropic materials, $\vec{P} = \epsilon_0 \chi \vec{E}$, [128] where χ is the electric susceptibility. The material's response to $\vec{E}$ can therefore be written as

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} = \epsilon_0 \vec{E} + \epsilon_0 \chi \vec{E} = \epsilon_0 \epsilon_r \vec{E}, \quad (5.1)$$

where $\epsilon_r = 1 + \chi$ is the relative dielectric function (for simplicity the subscript r is not used in the remainder of the text). The material's response is dependent on the frequency ω of the incident light, i.e., the complex dielectric function reads $\tilde{\epsilon}(\omega) = \epsilon_1 + i\epsilon_2$, where ϵ_1 and ϵ_2 are the light dispersion and absorption, respectively. Light-matter interaction is also described by the complex index of refraction $\tilde{n} = n + ik = \sqrt{\tilde{\epsilon}}$, [128] where n and k are the refractive index and extinction coefficient, respectively.

During an ellipsometric measurement in reflection mode, linearly polarized light is used, which becomes elliptically polarized after being reflected off the sample surface (Fig. 5.3(a)). To describe this change in polarization, the reflectance is analyzed in the orthogonal s - p system, where s and p denote planes that are parallel and perpendicular to the plane of incidence, respectively.

Fig. 5.3: (a) Schematic illustration of an ellipsometric measurement. Linearly polarized light (with electric field vector $\vec{E}$) is reflected at sample surface. The light-matter interactions change the polarization of the light to elliptically polarization. p-plane and s-plane indicate the planes that are parallel and perpendicular to the plane of incidence, respectively. (b) Light interactions at an interface between two media (materials with indices of refraction n_1, n_2). Angles of incident (θ_i), reflected (θ_r), and transmitted (θ_t) light with respect to the interface normal are indicated.

The simplest case of an ellipsometric measurement refers to a semi-infinite vacuum/sample system (also referred to as two-phase system), where light is either reflected or absorbed (see Fig. 5.3(b) for a schematic illustration). Reflection then occurs at the interface of two media with indices of refraction $\tilde{n}_1$ and $\tilde{n}_2$ ($\tilde{n}_1 = 1$ in case of vacuum), and incident and transmitted light have the angles θ_i and θ_t with reference to the interface normal, respectively. In this case, Snell's law is valid (i.e., $\tilde{n}_1 \sin(\theta_i) = \tilde{n}_2 \sin(\theta_t)$), and the Fresnel equations describe the reflection coefficients in the s-plane (r_s) and p-plane (r_p), [129]

$$r_s = \frac{\tilde{n}_1 \cos(\theta_i) - \tilde{n}_2 \cos(\theta_t)}{\tilde{n}_1 \cos(\theta_i) + \tilde{n}_2 \cos(\theta_t)}, \quad r_p = \frac{\tilde{n}_1 \cos(\theta_t) - \tilde{n}_2 \cos(\theta_i)}{\tilde{n}_1 \cos(\theta_i) + \tilde{n}_2 \cos(\theta_t)}. \quad (5.2)$$

These quantities are complex numbers and define the complex reflectance ratio ρ_{ref} as [129]

$$\rho_{ref} \equiv \frac{r_p}{r_s} \equiv \tan(\Psi) \exp(-i\Delta). \quad (5.3)$$

In Eq. 5.3, Ψ and Δ are the amplitude ratio and the phase difference of the reflection coefficients, respectively, which are the measured ellipsometric quantities. Recalling $\tilde{n} = \sqrt{\tilde{\epsilon}}$ and Snell's law, the dielectric function $\tilde{\epsilon}$ of medium 2 (i.e., the material under investigation) can be calculated:

$$\tilde{\epsilon} = \tilde{\epsilon}_1 \sin^2(\theta_i) + \frac{(1 - \rho_{ref})^2 \sin^2(\theta_i) / \tan^2(\theta_i)}{(1 + \rho_{ref})^2}, \quad (5.4)$$

where $\tilde{\epsilon}_1$ is the dielectric function of medium 1 (i.e., vacuum).

If thin films are investigated via ellipsometry (i.e., a three-phase system comprising of vacuum, transparent film, and semi-infinite substrate), light that is transmitted through the film interacts with the film/substrate interface, and multiple reflections occur. For a single film with thickness h_f on a substrate that is probed with light with wavelength λ , the Fresnel reflection coefficients read

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$$r_{123s} = \frac{r_{12s} + r_{23s} \exp(i2\beta)}{1 + r_{12s}r_{23s} \exp(i2\beta)}, \quad r_{123p} = \frac{r_{12p} + r_{23p} \exp(i2\beta)}{1 + r_{12p}r_{23p} \exp(i2\beta)}, \quad (5.5)$$

where

$$\beta = \frac{2\pi h_f \tilde{n}_2 \cos(\theta_t)}{\lambda}. \quad (5.6)$$

In Eqs. 5.5 and 5.6, the subscripts 1,2,3 denote vacuum, transparent film, and semi-infinite substrate, respectively. Combining Eqs. 5.2 through 5.6 (note that here, $\rho_{ref} = r_{123p}/r_{123s}$), the pseudo-dielectric function $\langle \tilde{\epsilon} \rangle$ that contains all optical information of the three media and the film thickness can be computed from Eq. 5.4.

Additional analysis and modelling of the measured pseudo-dielectric function is required to determine the optical response (i.e., dielectric function) and thereby intrinsic properties (e.g., electron density, and mean-free-path of electrons in a metal) of the film under investigation. This is done by using models that allow computing the optical response of the measured system, which may be purely mathematical with no physical meaning, or founded on classical/quantum mechanical descriptions of optoelectronic properties of materials. Within the present thesis work, two models are used for analysis of ellipsometric data, the Lorentz and Drude models that are outlined in the following.

Lorentz oscillator

The Lorentz oscillator describes the response of electrons (with effective electron mass m_e , and charge $-e$), which are bound to a positive ion core, to an electric field $\vec{E}(\omega) = \vec{E}_0 \exp(-i\omega t)$, where ω and t are frequency and time, respectively. The motion of electrons in one dimension (i.e., x) is described by [129]

$$m_e \frac{d^2x}{dt^2} = -m_e \Gamma_L \frac{dx}{dt} - m_e \omega_0^2 x - e \vec{E}_0 \exp(-i\omega t), \quad (5.7)$$

where the first term on the right hand side accounts for energy loss mechanisms in electronic transitions with the damping constant Γ_L (also called *broadening*), the second term represents the restoring force with the resonance frequency ω_0 , and the third term is the electrostatic force due to the external electric field $\vec{E}$. Solving the differential equation gives

$$\vec{x}(\omega) = -\frac{e \vec{E}(\omega)}{m_e(\omega_0^2 - \omega^2 - i\Gamma_L \omega)}. \quad (5.8)$$

The induced polarization by this motion of charge carriers is $\vec{P}(\omega) = -ne\vec{x}(\omega)$, where n is the number of electrons per unit volume. Recalling $\epsilon_0 \vec{E} + \vec{P} = \epsilon_0 \tilde{\epsilon} \vec{E}$ allows calculation of the dielectric function for a Lorentz oscillator

$$\tilde{\epsilon}_L(\omega) = 1 + \frac{ne^2}{\epsilon_0 m_e} \frac{1}{(\omega_0^2 - \omega^2 - i\Gamma_L \omega)}. \quad (5.9)$$

A derivation of the dielectric function from quantum mechanical point of view gives formally the same result; in this case ω_0 corresponds to the frequency of an electron transition between two states separated by the energy $\hbar\omega_0$. [130] In a real material, multiple electron transitions are possible, e.g., interband transitions in a material triggered by the energy of the incident light. In addition, experimental setups have a finite range of frequencies that are probed, while transitions that occur at higher frequencies lie outside the experimental range still influence the optical response of the material. These effects are included in the Lorentz model via the parameter ε_∞ and the dielectric function $\tilde{\varepsilon}_L(\omega)$ for the case of multiple oscillators reads

$$\tilde{\varepsilon}_L(\omega) = \varepsilon_\infty + \frac{ne^2}{\varepsilon_0 m_e} \sum_i \frac{f_i}{\omega_{0,i}^2 - \omega^2 - i\Gamma_{L,i}\omega}. \quad (5.10)$$

In Eq. 5.10, f_i is called oscillator strength, and accounts for the relative probability of quantum mechanical transition.

The Lorentz model is used to describe the optical response of metal films on insulators during initial growth stages. In the island-stage of film formation, the film supports *localized surface plasmon resonance* (LSPR), [40,129] i.e., electrons in the isolated islands are in-phase with the externally applied electric field, and move collectively. This induces an electric dipole locally that is opposing the external field. Owing to the dipole, a restoring force exists, and the resulting electron oscillation has a resonance frequency. The presence of the island surface and ions leads to damping of the oscillations. This resonance effect can be modelled with one Lorentz oscillator, with ω_0 and Γ . LSPR is described with a single oscillator as long as the island shape can be approximated by hemisphere, and island-island interactions are negligible, i.e., when the island spacing is larger than the interaction distance between the electric dipoles. [129]

Drude oscillator

The Drude model is based on Drude's free electron theory that describes ideal metals, i.e., metals in which the optoelectronic response is only determined by unbounded electrons. In the Drude model, conduction band electrons are free, i.e., no restoring force exists, and Eq. 5.7 is reduced to

$$m_e \frac{d^2x}{dt^2} = -m_e \Gamma_D \frac{dx}{dt} - e\vec{E}_0 \exp(-i\omega t). \quad (5.11)$$

The solution of Eq. 5.11 and treatment as for the Lorentz model give the dielectric function for the Drude model

$$\tilde{\varepsilon}_D(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma_D\omega}, \quad (5.12)$$

where $\omega_p = \sqrt{ne^2/(\varepsilon_0 m_e)}$ is the plasma frequency. [128] From ω_p and Γ_D , the film resistivity can be calculated as $\rho_{res} = \Gamma_D \varepsilon_0^{-1} \omega_p^{-2}$. A description of film growth with the Drude model is valid for percolated and continuous metal films. The time

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evolution of ρ_{res} can also be used to determine the continuous film formation thickness, since ρ_{res} is in a steady-state for continuous films, as illustrated in Fig. 5.4. [131]

Fig. 5.4: Evolution of film resistivity vs. film thickness as determined from *in situ* spectroscopic ellipsometry using a Drude model to simulate a metal film. The continuous film formation thickness is indicated with a vertical solid arrow.

Spectroscopic ellipsometry measurements performed in course of this thesis work are performed and analyzed as follows:

- Loading of Si substrates (thickness $625 \mu\text{m}$, i.e., semi-infinite) covered with thermally grown SiO_2 , and measurement of Ψ and Δ as function of incident-light photon energy $\hbar\omega$.
- Fitting of $\Psi(\omega)$ and $\Delta(\omega)$ to three-phase model (i.e., vacuum/ SiO_2 /Si stack), in which the dielectric functions of SiO_2 and Si are taken from databases, [132] and incidence angle θ_i and SiO_2 layer thickness are fitting parameters. θ_i is fitted since it can vary from nominal incidence angle defined by the chamber geometry due to sample mounting and sample holder loading.
- Real-time measurement of $\Psi(\omega, t)$ and $\Delta(\omega, t)$ during film growth.
- Fitting of *in situ* data to model (i.e., vacuum/film/ SiO_2 /Si) where the film is simulated by a single Lorentz oscillator (accounting for LSPR in the island stage of film formation), and a Drude oscillator (accounting for ideal metal behavior in percolated and continuous films). Fitting parameters are f , ω_0 , and Γ_L from the Lorentz term, ω_p and Γ_D from the Drude term, as well as ε_∞ and h_f .
- From the film thickness h_f vs. time t evolution, the deposition rate is determined as dh_f/dt , which is constant in continuous films.

In situ spectroscopic ellipsometry is employed in Papers III and IV, where the microstructural evolution of Ag films on SiO_2 /Si substrate is investigated during growth in various Ag- N_2 and Ag- O_2 atmospheres, respectively. In Paper V, growth of AgCu films with various compositions is observed with *in situ* spectroscopic ellipsometry.

5.2.2. Substrate curvature measurement

Stress generation mechanisms during thin film growth are discussed in Chapter 4. The investigation of stress during growth is based on the substrate curvature technique, which measures changes in the curvature of a film-substrate system in real-time. When stress forms in the film, the stress is transferred to the substrate, which bends if the transferred force is large enough. Figures 5.5(a) and (b) show the conventional description of the substrate curvature: If the film is under compression, the substrate curvature κ is negative, and for tensile stress in the film, κ is positive.

Fig. 5.5: Schematic illustration of the curvature (κ) change of the substrate (light grey) when the film (dark grey) is (a) under compressive stress and (b) under tension. (c) Schematic illustration of the substrate curvature technique; laser spots with spacing d_0 are reflected on the curved substrate (incidence angle α) and observed with a camera. If during film deposition stress forms in the film, the substrate curvature changes, and the measured spacing changes with time $d(t)$.

The substrate curvature is measured by tracing the spacing of a 3×3 array of laser spots (wavelength 658 nm), which are reflected off the substrate surface, with a CCD camera. A schematic illustration of the substrate curvature setup is presented in Fig. 5.5(c), where d_0 is the initial spacing, α is the incidence angle, and $d(t)$ indicates that the spacing changes with time t (i.e., during film deposition). The change in substrate curvature with time $\Delta\kappa(t)$ is calculated as

$$\Delta\kappa(t) = \frac{\Delta d(t) \cos(\alpha)}{d_0 2L}, \quad (5.13)$$

where $\Delta d(t) = d(t) - d_0$, and L is the distance between substrate and camera.

For a correct application of the substrate curvature technique, the lateral dimensions of the substrate have to be large compared to substrate and film thickness, and the film thickness must be small ($< 1\%$) compared to the substrate thickness h_s . This is ensured by using $1 \times 1 \text{ cm}^2$ substrates, compared to $h_s \cong 100 \text{ }\mu\text{m}$ and film thicknesses in the nm range. Moreover, several hypotheses about the mechanical state of the film/substrate system apply: [133,134]

- (i) The system has a neutral plane that is not deformed during bending of the substrate.
- (ii) Only biaxial stress is observed, transversal stress is negligible.
- (iii) The substrate is homogeneous and isotropic, and the film material is isotropic.
- (iv) Linear elasticity can be applied.
- (v) The observed curvatures are small.

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As deposited films are very thin, transversal stresses are negligible, satisfying hypothesis (ii). Point (iii) is ensured by using Si(100) single-crystal substrates. Investigated films are pure metal films (Ag, Cu), which do not support large enough stresses to lead to conditions dissatisfying points (iv) and (v).

The relation between the change of the substrate curvature to film stress was developed by Stoney [135] and reads

$$\Delta\kappa = \frac{6 \Delta(\bar{\sigma} \times h_f)}{Y_S h_S^2}, \quad (5.14)$$

where $\bar{\sigma}$ is the average film stress, h_f is the film thickness, and Y_S is the substrate biaxial modulus. In the original Stoney equation, the elastic modulus is used, which was later corrected by Hoffman. [136] This equation allows the determination of the change of the stress-thickness product $\Delta(\bar{\sigma} \times h_f)$, when the substrate properties Y_S and h_S are known. It is noted that $\Delta(\bar{\sigma} \times h_f)$ is equivalent to the force per unit width, which is used in figures in Chapter 4.

Equation 5.14 implies that only the average in-plane film stress is measured via the substrate curvature technique, i.e., no information about the lateral stress distribution is given. By defining $\bar{\sigma}$ as

$$\bar{\sigma} = \frac{1}{h_f} \int_0^{h_f} \sigma_{xx}(z) dz, \quad (5.15)$$

where σ_{xx} is the in-plane stress, the evolution of the stress with film thickness can be computed. Since the substrate curvature technique is used *in situ*, the stress evolution with time is given as

$$\frac{d(\bar{\sigma} \times h_f)}{dt} = \sigma_{xx}(h_f) \frac{dh_f}{dt} + \int_0^{h_f} \frac{\delta\sigma_{xx}(z)}{\delta t} dz. \quad (5.16)$$

The first term in Eq. 5.16 represents the stress formed in the topmost layer of the film, i.e., the *incremental* or *instantaneous* stress, while the second accounts for stress changes in the bulk of the film. When interpreting stress data that is acquired with the substrate curvature technique, Eq. 5.16 must always be considered, since changes in the stress state can result both from the top layer or the bulk of the film.

In practice, an *in situ* substrate curvature measurement gives $\Delta\kappa$ vs. t data. Former quantity is used to calculate the stress-thickness product with Eq. 5.14 (h_S is determined for each substrate after deposition), while the (nominal) film thickness is calculated from t with the deposition rate. This gives $\bar{\sigma} \times h_f$ vs. h_f data that is discussed in detail in Chapter 4.

The substrate curvature technique is used in Paper I to determine continuous film formation thicknesses of Ag and Cu films on amorphous carbon, as function of deposition rate and substrate temperature. The stress evolution of these film/substrate systems, determined from substrate curvature measurements, is discussed in Paper II. Paper VI presents the evolution of stress during the growth of Ag films in mixed Ar-N₂ atmospheres.

5.2.3. Four-point-probe measurement

The four-point-probe (4PP) measurement allows for determining the resistivity of a film/substrate system by measuring the voltage drop V between two probes on the sample surface, when applying an electric current I to two additional probes. If the placement of the four contacts is symmetric, and the sample is homogeneous and without holes, the van der Pauw theorem can be applied [137] and the film sample resistivity ρ is calculated as

$$\rho = \frac{\pi h_f}{\ln(2)} \frac{V}{I}. \quad (5.17)$$

The term $\pi/\ln(2)$ in Eq. 5.17 is a geometric correction factor that accounts for the finite sample thickness, the probe position with respect to the sample edge, and the finite lateral size of the sample. [137] Forming the sheet resistance $R_S = \rho/h_f$, a sample-independent parameter is provided, i.e., sheet resistance data of samples with the same geometry can be easily compared.

Measuring the electrical resistivity of a growing film allows for obtaining information about the film morphological evolution, e.g., when depositing a conductive material onto insulating substrates, a characteristic resistivity drop can be seen when the film becomes macroscopically conductive, i.e., at the *percolation thickness*. For such investigations, a load-lock compatible system for 4PP measurements was developed by Colin *et al.* [56] (see Fig. 5.6(a)) that measures the sheet resistance of the film/substrate system *in situ* and in real-time. The sample holder of the system is presented in Fig. 5.6(b), which also shows the mask that protects electric contacts from film deposition. Prior to sample mounting, gold contacts are deposited onto the silicon substrate with a titanium adhesion layer, to ensure a uniform contact during measurement. These contacts can be square ($2.5 \times 2.5 \text{ mm}^2$) or rectangular ($2.5 \times 10 \text{ mm}^2$), which does not affect the quality of the measurement (in case of rectangular contacts, one voltage and one current probe is placed on each contact). [56]

Fig. 5.6: (a) Schematic illustration of the four-point-probe measurements setup used for *in situ* resistivity measurement in a high-vacuum deposition chamber. (b) Sample holder used for the four-point-probe measurement. A mask (1) protects the copper contacts (2) that hold the substrate in place. Four squares or two gold stripes (3) are deposited onto substrates prior to film deposition that act as ohmic contacts. Copper contacts are connected to vertical silver rods on springs (4) that transfer current/voltage to the mounting system. The sample holder is mounted on a Teflon insulating plate (5) that is fixed onto the base (6). Reprinted with permission from Ref. [56].

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Figure 5.7 presents data obtained from *in situ* 4PP measurements during Ag film growth on SiO_2 substrates, where h_f is calculated by multiplying time with the deposition rate. Plotting R_s vs. h_f in logarithmic scale (see Fig. 5.7(a)) shows a sudden drop by several orders of magnitude from high R_s , which corresponds to the percolation of the film. This characteristic thickness is obtained more accurately from $R_s \times h_f$ vs. h_f data (see Fig. 5.7(b)), which starts at zero for $h_f = 0 \text{ nm}$. [56] Furthermore, the thickness at which a continuous film is formed can be, theoretically, determined from the minimum of the R_s vs. h_f data (compare to resistivity vs. film thickness data in Fig. 5.4, obtain from *in situ* spectroscopic ellipsometry). However, this is not possible with the setup used in the present work due to insufficient signal-to-noise ratio.

In situ 4PP measurements are presented in Paper I, where they are used to determine percolation thicknesses of Ag and Cu films on amorphous carbon, as function of deposition rate and substrate temperature.

Fig. 5.7: Evolution of (a) sheet resistance R_s and (b) sheet resistance-film thickness product $R_s \times h_f$ vs. film thickness h_f for deposition of Ag on amorphous carbon/ SiO_2 substrate. The percolation thickness is indicated with vertical lines.

5.2.4. *Residual gas analysis*

Residual gas analysis is a technique that allows the determination of the composition of the chamber atmosphere at base pressure or during film deposition. Former measurement is of interest, as contamination from the background pressure can lead to changes in the film morphology, and latter is used to determine the species in the plasma, and the ratios of working gases, if several gases are used (e.g., argon and nitrogen, argon and oxygen).

Every residual gas analyzer (RGA) consists of three parts, the ionization unit, the mass filter, and the detector. Ionization of gas molecules is needed, since mass filtering is performed in electric fields (i.e., neutral species cannot be distinguished), as well as increasing the sensitivity of the measurement. [21] Gas molecules are typically ionized via collision with electrons that are created in a cathode (ionization process $e^- + A \rightarrow A^+ + 2e^-$). This ionization process is one source for measurement errors, since collision cross-sections of gas molecules and electrons depend on the gas species, [21] i.e., ionization of species with small cross-sections is less probable, which leads to an under-representation of these species in the detected signal.

The positive ions are then accelerated toward the mass filter, which filters ions with respect to their mass-to-electric charge ratio M/z . Figure 5.8(a) illustrates a quadrupole mass filter. When passing through the positively charged electrodes (direct current (DC) potential $U > 0$), a positive ion has a stable trajectory (Fig. 5.8(b)); this trajectory is destabilized when applying an additional radio frequency (RF) potential $V\cos(\omega t)$, with $V > U$, to the electrodes (Fig. 5.8(c)). Ions with small M/z values are deflected by the Lorentz force created due to the resulting potential $U + V\cos(\omega t)$ and do not pass the filter (i.e., ions collide with electrodes), while ions with large M/z values pass, i.e., the positively charged electrodes act as high-pass filter (Fig. 5.8(d)).

A positive ion is attracted by the negatively charged electrodes (DC potential $-U$) and does not pass the quadrupole filter (Fig. 5.8(e)). When superposing the RF potential $V\cos(\omega t)$, ions with small M/z values pass the filter (Fig. 5.8(f)), i.e., the negatively charged electrodes act as low-pass filter. As only ions that pass both filters are detected, the quadrupole is a band-pass filter. Ions that pass the mass filter are detected in an ion current detector (comparable to ion gauges described in Chapter 2). Different M/z are probed by sweeping the DC and RF potentials linearly in time. Trajectories in Fig. 5.8 are simplified, in reality, the superposition of the electric fields leads to helical trajectories. [21]

Fig. 5.8: Schematic illustration of a quadrupole mass filter, (a) that consists of two pairs of electrodes at positive and negative direct current (DC) potential. Trajectories of positive ions due to (b) positive DC potential and (c) superposed radio frequency (RF) potential, which depend on mass-to-charge ratio M/z . (d) Signal measured at the detector as function of M/z ; the positive electrodes act as low-pass filter and the negative electrodes act as high-pass filter. Trajectories of positive ions due to (e) negative DC potential and (f) superposed RF potential.

Residual gas analysis was performed to determine the composition of the atmosphere at base pressure in both deposition chambers, an example for the species present in the UHV chamber at base pressure is presented in Fig. 5.9. The background pressure is created by hydrogen (H_2), carbo-hydrides (CH_x), traces of water (H_2O), carbon monoxide (CO), and dioxide (CO_2). Analysis in the HV-regime gives a similar result, with water as the most prominent constituent of the gas. In paper VI, this technique is used to determine the partial pressure of N_2 in a mixed Ar- N_2 working gas.

Fig. 5.9: Gas species detected in the ultra-high vacuum chamber at base pressure via residual gas analysis.

5.3. *Ex situ* characterization

Ex situ techniques described in this section were used for characterizing films with respect to their surface morphology, crystallography, and chemical composition, to better understand and analyze *in situ* obtained data. This is achieved by probing films with ultra-sharp tips (Section 5.3.1), electrons (Sections 5.3.2 through 5.3.4), x-rays (Sections 5.3.5 through 5.3.8), and ions (Section 5.3.9).

Prior to *ex situ* characterization, great care was taken to minimize changes in the film due to interaction with the atmosphere (e.g., oxidation, surface restructuring). This was obtained by depositing amorphous carbon capping layers onto films, before subjecting them to the atmosphere, and by performing measurements shortly after unloading, where possible. Carbon was chosen, because it does not have any chemical affinity to investigated silver and copper films, while its amorphous nature does not interfere with characterization techniques that investigate the film crystallography.

5.3.1. *Atomic force microscopy*

Atomic force microscopy (AFM), which belongs to the family of scanning probe microscopies, allows for real-space investigation of the surface topography of condensed matter. [138] Its principle setup is illustrated in Fig. 5.10(a). The electrostatic and van der Waals forces between the surface atoms of the probed material and a sharp tip lead to a deflection of the cantilever on which the tip is mounted. A laser is reflected on the backside of the cantilever, for measuring its deflection. Cantilever and tip are typically micromachined from silicon. [4] A surface topographical map is acquired by moving the cantilever over the sample surface with the help of piezoelectric crystals that are connected with the cantilever. The surface topography is typically presented in color maps (see Fig. 5.10(b)), and used to image the surface in real space.

Three measuring methodologies exist for AFM: [4] In contact-mode AFM, the tip is in close proximity to the surface, such that electrostatic repulsive forces from overlapping electron clouds lead to cantilever deflection. In non-contact-mode, the tip oscillates 1 – 10 nm from the sample surface. At such distances, van-der Waals forces attract the tip, which leads to changes in vibrational amplitude and resonance frequency. Tapping-mode is a combination of these two modes, where the amplitude of the cantilever oscillation leads to surface contact. AFM measurements presented in this work were performed in tapping-mode. The surface profile is obtained by keeping the tip-surface distance, the force on the tip, or the oscillation amplitude/frequency constant, which performed via a control loop between detector and piezo crystals.

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Fig. 5.10: (a) Schematic illustration of an atomic force microscopic measurement in tapping-mode. A sharp tip is mounted on a cantilever and interacts with the film surface. This leads to bending of the cantilever, which is detected by tracing the position of a laser spot that is reflected on the cantilever. (b) Surface profile of a silver thin film, height is represented in false color scale. (c) Evolution of height-height-correlation function $g(r)$ vs. lateral distance r . From this data, the roughness scaling factor α , lateral feature size d and root-mean-square surface roughness w can be determined.

For quantitative analysis of AFM images, the height-height correlation function $g(\vec{r}) = \langle [h(\vec{x} + \vec{r}) - h(\vec{x})]^2 \rangle$ is determined, [139] where $h(\vec{x})$ is the surface height at a position $\vec{x} = (x, y)$ on the surface, $\vec{r}$ is a displacement vector, and $\langle \dots \rangle$ denotes the statistical average over the entire surface. In Fig. 5.10(c), $g(\vec{r})$ vs. $\vec{r}$ data of the AFM image in Fig. 5.10(b) is presented. For small values of $\vec{r}$, $g(\vec{r}) \sim r^{2\alpha}$, where α is the roughness scaling exponent, while $g(\vec{r}) = 2w^2$ for large values of $\vec{r}$, where $w = \langle [h(\vec{x}) - \bar{h}]^2 \rangle^{1/2}$ is the root-mean-square surface roughness ($\bar{h}$ is the average surface height). These limits are indicated in Fig. 5.10(c); at the intersection of the limit functions, the correlation length d is defined, which corresponds to the average lateral feature size of objects present at the surface. Analysis of α , w and d with respect to growth time (i.e., film thickness), allows drawing conclusions about the evolution of the growth front, e.g., whether in-plane or out-of-plane growth is prominent. [140]

Surface topography images and analysis thereof of Ag and Cu films deposited at various deposition rates and substrate temperatures are presented in Papers I and II. Analysis of Ag films deposited in various working gas atmospheres (Ar and Ar-N₂) is presented in Paper VI.

5.3.2. Scanning electron microscopy

Scanning electron microscopy (SEM) is used for imaging the surface of a sample by probing it with an electron beam that is moved over the sample (i.e., the sample is scanned). Primary (i.e., beam) electrons have energies in the range of a few to tens of keV , i.e., the primary electron beam is created by accelerating electrons toward the sample in a kV -potential difference. Electron-matter interactions lead to emission of electrons and x-rays from the sample, which can be detected, and give information about the sample chemistry and topography. Figure 5.11(a) presents the teardrop-shaped volume from which emission stems. [4] The emission volume has a lateral size of $\sim 10\text{ nm}$ (i.e., the lateral resolution of SEM) and is larger than the primary electron beam ($\sim 1\text{ nm}$ diameter).

Secondary electrons are created by inelastic scattering when primary electrons interact with the sample electrons in the near-surface region ($\sim 1\text{ nm}$ depth), and have low energies in the eV -range (see Fig. 5.11(b)). As secondary electrons stem from the near-surface region, their intensity is strongly influenced by the surface topography of the sample, as illustrated by Fig. 5.11(c). If the primary electron beam hits the surface with a high incidence angle, a larger portion of the interaction volume is close to the surface, and more secondary electrons are emitted. Backscattered electrons are created by elastic scattering and have energies that are close to primary electrons. The probability of backscattering increases with the atomic number of the sample material, i.e., a compositional contrast can be observed from backscattered electron images, however, quantitative chemical analysis is not possible. Diffraction of backscattered electrons is used for microstructural analysis (see Section 5.3.4).

Fig. 5.11: (a) Interaction volume of matter with electron beam from which electrons and x-rays are emitted. (b) Energy distribution of emitted electrons as function of emission process. (c) Effect of surface topography on the emission of electrons. Reprinted with permission from Ref. [4].

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Electron-matter interactions lead to further emission processes that are not used for imaging purposes, and they are briefly outlined in the following: The collision of primary electrons in the sample can cause vacant electronic states in the inner electron shells, which outer-shell electrons can occupy. The energy that is released by this relaxation is emitted in form of x-rays that have characteristic energies for the relaxation process, i.e., these x-rays can be used for chemical analysis (see Section 5.3.8 for more details). In some cases, the relaxation can instead lead to the emission of an outer-shell electron (i.e., *Auger* electron), which can be used for compositional analysis due to characteristic energy levels.

SEM imaging is performed on discontinuous Ag and AgCu films on SiO₂/Si substrates to determine lateral island sizes, island size distribution and substrate area coverage in Papers IV and V, respectively.

5.3.3. *Transmission electron microscopy*

If an electron beam interacts with a thin sample, the attenuation by the sample is weak, and the electron beam is partially transmitted. In transmission electron microscopy (TEM) the transmitted electron beam is analyzed. Compared to SEM, higher acceleration voltages are applied in TEM (hundreds of kV), and sample preparation is essential (sample thickness $< 100\text{ nm}$). [4,141] Electrons can be scattered elastically by the ion cores of the sample, which gives information about the film thickness, elemental composition, and crystal structure. Latter stems from diffraction of electrons at crystallographic planes. Inelastic scattering occurs on microstructural features on the sample (e.g., grain boundaries, pores, dislocations, and defects), which leads to local intensity fluctuations.

During *bright field imaging*, the central electron beam is observed, while all diffracted beams are excluded by placing apertures in the back focal plane of the objective lens. With this imaging mode, the sample microstructure can be investigated. *Dark field imaging* is better suited to observe local crystallographic features (e.g., dislocations), as the intensity of one diffracted electron beam is analyzed. When analyzing the electron intensities at the back focal plane, microdiffraction patterns are observed (i.e., *selected area electron diffraction* SAED), which give information about the local structural features (e.g., lattice orientation). In this case, TEM is used as an analytical instrument.

TEM is a powerful tool for analysis at the nanoscale, since it has a lateral resolution in the sub- nm range. Limitations are caused by the quality of electron lenses, which cause aberration; modern electron microscopes are aberration-corrected. [141] For the analysis of thin films, cross-sectional TEM (XTEM) can be performed, i.e., the film is imaged perpendicular to its growth direction. This gives information about the film morphology as function of the film thickness, e.g., close to the film/substrate interface, and the surface.

Plan-view TEM images of discontinuous Ag films deposited onto electron-transparent SiO_2 grids are presented in Paper III, from which island size and distance distributions are determined. XTEM and SAED are used to analyze continuous Ag films deposited in Ar and Ar- N_2 atmospheres in Papers III and VI.

5.3.4. *Electron backscatter diffractometry*

Electron-matter interactions lead to incoherent scattering of an electron beam in the sample. These incoherent scattering processes are sources of electrons within the sample, and electrons that are scattered toward the sample surface (i.e., backscattered), may be scattered coherently by the crystal lattice before reaching the surface, carrying information about the sample crystal structure. Electron backscatter diffractometry (ESBD) is a technique that analyses the resulting diffraction patterns. [142] Electrons that are elastically scattered in a three-dimensional crystal lattice travel along trajectories that form a pair of cones (i.e., Kikuchi or Kossel cones) with an axis that is perpendicular to the diffracting plane, and an opening angle that is related to the Bragg diffraction angle (see Fig. 5.12(a) for geometry, and Section 5.3.5 for more detailed information about diffraction). Imaging of this electron beam on a planar detector leads to hyperbolic bands of intensity known as *Kikuchi bands*. Each crystallographic orientation leads to specific bands (i.e., defined by cone axis and opening angle), and the intersection of Kikuchi bands on the detector is used for the analysis on the EBSD data (Fig. 5.12(b)). By comparing Kikuchi band widths and intersections to computed data for ideal crystal lattices, the crystal orientation of the probed volume can be attributed. By scanning the primary electron beam over the sample surface, grain orientation maps can be created, from which grain sizes can be determined.

EBSD maps of Ag and Cu films deposited at various deposition rates and substrate temperatures are presented in Paper II, where they are used to determine lateral grain sizes and orientations. In Paper VI, EBDS maps of Ar- and Ar-N₂-grown Ag films are presented for grain size and orientation analysis.

Fig. 5.12: (a) Creation of Kikuchi cone (with opening angle θ) during electron diffraction in a three-dimensional crystal lattice, and formation of Kikuchi bands on a planar detector. (b) Schematic illustration of signal detected via electron backscatter diffractometry of a polycrystalline sample. Bands do not appear hyperbolic due to small detector size.

5.3.5. X-ray diffractometry

Diffraction is a phenomenon that occurs when photons interact with structures that have sizes comparable to the photon wavelength λ . Microstructural features of condensed matter (e.g., the lattice parameter in crystals) are typically in the sub- nm range and can therefore be analyzed by photons with wave lengths in this range, i.e., x-rays. In x-ray diffractometry (XRD) photons are created in metal anodes (typically copper anode; $\lambda = 0.154\text{ nm}$), interact with a sample, and are detected after scattering. Elastic scattering of x-rays in randomly ordered matter, or matter with only short-range order (i.e., amorphous materials), leads to destructive interference. Concurrently, in materials with long-range order, scattering on parallel planes of atoms can lead to constructive interference.

The long-range order in crystalline materials can be described by unit cells, which are defined by the lengths a, b, c of the unit cell axes, and angles α, β, γ between the b and c , a and c , and a and b axes, respectively. The complete crystal lattice is formed by translating the unit cell in all three dimensions. For cubic lattices that are discussed in this work, $a = b = c$, and $\alpha = \beta = \gamma = 90^\circ$. Miller indices hkl define planes and positions in the unit cell; in a cubic lattice with the lattice parameter a , the spacing d_{hkl} of the plane (hkl) is calculated as

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (5.18)$$

The crystal symmetry can also be described in the reciprocal space, where each plane corresponds to a reciprocal vector with norm $2\pi d_{hkl}^{-1}$ that is orthogonal to the real-space plane. [142,143]

Let $\vec{k}$ and $\vec{k}'$ be the wave vectors of incident and scattered photons, respectively, where $|\vec{k}| = |\vec{k}'| = 2\pi\lambda^{-1}$, and θ the angle between the wave vectors and the surface of the reflecting sample (see Fig. 5.13). Then, the scattering vector $\vec{Q} = \vec{k}' - \vec{k}$ has the norm $4\pi\lambda^{-1}\sin(\theta)$ and is orthogonal to the plane. Scattering occurs on a plane, when the scattering vector is equal to the reciprocal vector, i.e., $4\pi\lambda^{-1}\sin(\theta) = 2\pi d_{hkl}^{-1}$. Rearranging this equation gives the condition for Bragg diffraction $2d_{hkl}\sin(\theta_B) = \lambda$, where θ_B is the Bragg diffraction angle. [142,143]

Fig. 5.13: Bragg diffraction of an incident x-ray beam on a crystalline sample in the reciprocal space.

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Bragg's law describes at which angles diffraction peaks can be expected. The intensity of peaks depends on further parameters, most importantly on the structure factor F that depends on the position of atoms within the unit cell. If the unit cell contains multiple atoms, scattering of photons on different atoms in the unit cell can lead to destructive interference. The structure factor for the (hkl) plane is calculated as

$$F_{hkl} = \sum_j f_j \exp(2\pi i[hu_j + kv_j + lw_j]), \quad (5.19)$$

where j is the number of atoms in the unit cell, f_j are atomic scattering factors, and u_j, v_j, w_j denote the position of the atom j in the unit cell. The effect of F can be illustrated by the face-centered cubic (fcc) lattice of silver (or copper), where $j = 4$, and $f_j = f$ for all atoms. Atom positions are $[0,0,0]$, $[\frac{1}{2}, 0, \frac{1}{2}]$, $[\frac{1}{2}, \frac{1}{2}, 0]$, and $[0, \frac{1}{2}, \frac{1}{2}]$, i.e.,

$$F_{hkl} = f \times [1 + \exp(\pi i[h + l]) + \exp(\pi i[h + k]) + \exp(\pi i[k + l])]. \quad (5.20)$$

Equation 5.20 gives $F_{hkl} = 4f$ for planes in which h, k , and l are all even (including 0) or uneven, and $F_{hkl} = 0$ for planes with mixed h, k, l , e.g., the 100 reflection is forbidden, while the 111 can be measured.

In a powder sample, the Bragg condition can be fulfilled by planes with different (hkl) at the same time; for cubic crystals this is the case as long as $h^2 + k^2 + l^2$ gives the same result, e.g., (111) and (-111) planes. Not all planes have the same representation within the unit cell, e.g., in the fcc lattice, eight planes of the $\{111\}$ family exist, while the $\{100\}$ family only has six, i.e., the intensity the 111 peak will be higher. The multiplicity factor accounts for this difference.

The derivation of the diffraction condition is only valid in an infinite crystal lattice. If the crystal size is finite, intensity peak broadening can be observed, i.e., with decreasing crystal size, the width of diffraction peaks increases. Peak broadening is also affected by microstrain in the crystallites. Determining the full-width-at-half-maximum ($FWHM$) of diffraction peaks allows estimating the size L of coherently diffracting domains in the sample via $FWHM = K\lambda/(L \cos(\theta_B))$. [144] K is a constant that accounts for the crystallite shape, and is close to unity (typically $K = 0.9$ is chosen). Note that this equation (known as Scherrer's equation) neglects microstrain, so it gives a lower limit of crystallite size.

For determination of the $FWHM$, experimental data can be fitted to mathematical models. [145,146] The Cauchy-Lorentz distribution function describes peak broadening due to the finite crystallite size well, while the Gauss distribution function is well suited to describe peak broadening due to local lattice parameter changes (i.e., microstrain). A convolution of these two functions is used in the Voigt distribution function; the Pseudo-Voigt function is a linear combination of Cauchy-Lorentz and Gauss distribution, which is easier to implement mathematically. [145]

XRD measurements presented in publications related to this thesis are performed in Bragg-Brentano geometry, i.e., x-ray source and detector are at fixed distance from the sample (see Fig. 5.14(a)). In $\theta/2\theta$ measurements, the scattering vector is always perpendicular to the sample surface, i.e., only crystal planes that are parallel to the substrate surface are probed. This is achieved by rotating source and detector by angles θ and $-\theta$, respectively, while the sample position is fixed, or by rotating sample and detector by θ and 2θ , respectively, while the x-ray source remains at fixed position.

A typical x-ray diffractogram of a silver thin film is presented in Fig. 5.14(b). Within the experimentally probed diffraction angles 2θ , two intensity maxima are observed, while the intensity is small for other angles (i.e., instrumental background). If peak positions correspond to reference peak positions obtained from powder diffraction samples, [147] the diffraction pattern can be attributed to a phase. Comparison of the integrated intensities I_{hkl} of measured peaks to the intensities $I_{hkl,0}$ of the reference data gives information of *texture* in the film, i.e., an overpopulation of certain crystallographic orientations with respect to the measurement geometry. The texture coefficient $TC(hkl)$ is calculated as

$$TC(hkl) = \frac{I_{hkl}/I_{0,hkl}}{\frac{1}{N} \sum_N I_{hkl}/I_{0,hkl}}, \quad (5.21)$$

where N is the number of considered diffraction peaks. $TC(hkl) = 1$ if the hkl orientation is represented as in a powder sample, $TC(hkl) > 1$ signifies an overpopulation, and $TC(hkl) < 1$ an underpopulation.

Fig. 5.14: (a) X-ray diffraction measurement in Bragg-Brentano geometry. In a $\theta/2\theta$ measurement, the scattering vector $\vec{Q}$ is perpendicular to sample surface, while x-ray source and detector rotate. (b) Schematic x-ray diffractogram of a silver thin film. The peak positions and relative intensities of 111 and 200 planes in a reference powder sample are indicated.

XRD measurements are performed on Ag thin films to determine texture and crystallite sizes in papers III through VI.

5.3.6. X-ray reflectometry

X-ray reflectometry (XRR) is an x-ray based characterization technique that allows determination of sample density and surface roughness, and, in case of supported thin films, also film thickness and interface roughness, by fitting reflectivity vs. scattering angle data to a mathematical model. [148] Figure 5.15 outlines schematically the geometry during an XRR measurement: The incident beam is reflected on the sample surface and partially transmitted into the sample. In case of a homogeneous sample, the transmitted photons are absorbed by the sample and lost for analysis. If a film/substrate system is measured, photons are reflected at the film/substrate interface and can be detected. The nature of interference between directly reflected photons and photons that were reflected at the interface depends on the film thickness h_f and the scattering angle θ . [148]

Fig. 5.15: Reflection of an x-ray beam from the surface of a thin film and from the film/substrate interface.

Figure 5.16 presents reflectivity vs. scattering data for bulk and thin film samples that was modeled. Three general regimes can be observed in the bulk model (see Fig. 5.16(a); bulk material is silver): (i) For $\theta < \theta_{crit}$, where θ_{crit} is the critical angle, total external reflection occurs, (ii) for $\theta > \theta_{crit}$, a decrease in intensity is observed, and (iii) for $\theta \gg \theta_{crit}$, a constant, very small reflectivity is measured, which corresponds to the background signal of the instrument. The critical angle is proportional to the square-root of the sample mass density. With increasing surface roughness, the intensity of the reflected beam decreases faster with scattering angle since more photons are lost to random scattering (compare surface roughness $w = 2 \text{ nm}$ vs. 1 nm Fig. 5.16(a)).

The presence of a film and the resulting multiple reflections at the film/substrate interface alters the XRR signal considerably. Figures 5.16(b) and (c) present reflectivity curves for Ag/SiO₂ stacks. We note that the θ_{crit} strongly depends on the film material, while the substrate has a weaker influence (compare positions of θ_{crit} in Fig. 5.16(a) and (b)). Fringes in the reflectivity data are a result of the constructive (local maxima) and destructive (local minima) interference of photons that are reflected at the surface and interface. Surface roughness leads to loss of coherency of photons, and fringes are not visible at high scattering angles; with increasing surface roughness, this fringe-diminution appears at lower scattering

angles (Fig. 5.16(b)). From the distance of the local maxima, the film thickness can be determined, i.e., fringes are closer to one another for thicker films (Fig. 5.16(c)).

For multilayer systems, intensity fluctuations of multiple interfaces overlap and create a complex pattern, however, data can be modelled with film density, film thickness, and interface roughness as fitting parameters. [149] This allows non-destructive measurement of these parameters, which is of great interest in materials research and quality control.

XRR is used in all papers related to this thesis. In Papers I, II and VI film thicknesses determined by XRR are used to calculate/verify deposition rates. In Papers III through V, XRR is used to verify film thicknesses determined by spectroscopic ellipsometry and calculate film densities and surface/interface roughness.

Fig. 5.16: Evolution of the reflectivity with scattering angle for (a) a bulk silver surface with surface roughness w , (b) a silver thin film with film thickness $h_f = 25 \text{ nm}$ and varying values of w , and (c) a silver thin film with $w = 1 \text{ nm}$ and varying values of h_f . Films are modeled on silicon dioxide substrate ($w = 0.1 \text{ nm}$), the critical angle of the models is indicated. Curves in (b) and (c) are shifted vertically for clarity.

5.3.7. X-ray photoelectron spectroscopy

The interaction of photons with matter can lead to emission of electrons (i.e., *photoelectrons*). X-ray photoelectron spectroscopy (XPS) analyses the kinetic energies of the emitted electrons, gaining information about the electron bonding state, i.e., XPS is a spectroscopic technique for chemical analysis (see schematics in Fig. 5.17). [150,151] Since only electrons from the near-surface region can leave the probed sample, it is a surface-sensitive technique (analysis depth in the *nm*-range).

The kinetic energy E_k of the photoelectron is the quantity that is measured in XPS, and it relates to the energy of the incident x-ray photon $\hbar\omega$ as [151]

$$E_k = \hbar\omega - E_B - \phi - \delta E. \quad (5.22)$$

In Eq. 5.22, the binding energy E_B is the quantity of interest in an XPS measurement, as it gives information about the local surrounding of the atom that the photoelectron was emitted from. ϕ is the spectrometer work function, an instrument constant that is known, and δE accounts for electrostatic charging of the sample surface, which is of importance for analysis of electrically insulating samples. Charging can be observed in the XPS data, since it affects all XPS peak uniformly, i.e. it is corrected by comparing the position of a known peak to its reference position found in databases.

Fig. 5.17: Schematic illustration of the photoelectron emission process: Interaction of a photon with energy $\hbar\omega$ with the sample leads to emission of an electron with kinetic energy E_k . Note spin orbital splitting in the *p* orbital.

Binding energies of electrons depend on the attraction of the positive ion cores in their vicinity. Compared to the elemental binding state, E_B increases if a stable compound is formed, and it decreases if the compound is metastable. If binding states are mixed (i.e., elemental and compound, or different compounds), XPS peak positions of these binding states overlap, and peaks have to be deconvoluted.

Interpretation of compound binding states is facilitated, since the change in E_B must be observable in XPS peaks of all elements that constitute the compound. When using XPS for chemical analysis, a detection limit of $\sim 0.1 - 1 \text{ at.}\%$ can be expected, where the upper limit is valid for light elements with few electrons. [4]

Spin orbital splitting occurs in all electron orbits except the s electrons. The spin states $+1/2$ and $-1/2$ lead to differences in E_B , i.e., XPS peak doublets are observed for these orbitals. For analysis, this is important when XPS peak broadening is larger than the E_B difference due to spin orbital splitting, and the doublet peaks overlap. A secondary loss feature of photoelectrons is plasmon losses induced by the collective movement of the electron cloud in the conduction band. Plasmon loss peaks are observed at energies higher than E_B .

XPS is used in Paper II to determine the concentration of contamination from the background pressure in the deposition chamber. In Papers III, IV and VI, concentration of gaseous species that are employed as surfactants is measured, and in Paper V, the composition of AgCu films that was determined from EDS measurements is verified.

5.3.8. *Energy-dispersive x-ray spectroscopy*

As mentioned in Section 5.3.2, x-rays are emitted from a sample when electrons from an outer shell fall into inner shells. The energy of the emitted photons is a fingerprint for the emitting atoms, i.e., by detecting the x-rays, chemical analysis is possible. Energy-dispersive x-ray spectroscopy (EDS) is often integrated in SEM, since the interaction of primary electrons with the sample, which is usually used for imaging, also creates x-rays, i.e., no additional instrument is needed. X-rays are detected in a Si(Li) photodetector, where they create electron-hole pairs in the depleted area of the reverse biased Si diode, which is detected as a voltage pulse. [4] Si(Li) detectors have an energy resolution of ~ 150 eV, which leads to the overlap of peaks in EDS spectra. The detection limit of elements is ~ 0.1 at. %. [4] X-rays stem from ~ 1 μm depth of the probed sample (see Fig. 5.11(a)), i.e., EDS is not very suitable for the analysis of thin films, however, it is used for qualitative analysis of the film composition.

EDS is used in Paper V to estimate the composition of AgCu films.

5.3.9. *Secondary ion mass spectrometry*

The principle of mass spectrometry was described in Section 5.2.4 for residual gas analysis. In secondary ion mass spectrometry (SIMS), an ion beam bombards the surface of a sample, which leads to the emission of neutrals and ions via sputtering processes, and once in the gas phase, ions are analyzed with respect to their mass-to-electric charge ratio M/z . [4] In time-of-flight SIMS (ToF-SIMS), M/z is determined by measuring the time that ions need to travel a defined distance. Since only sputtered ions are detected, SIMS is a surface sensitive technique with an analytical depth in the nm -range.

SIMS has an extremely low detection limit of $\sim 10^{-4}$ at. %, and is the most powerful characterization tool utilized within this thesis. A quantitative analysis of SIMS data is however only possible if a reference with known composition, and same morphological features (grain size, orientation, roughness) as the studied sample is available. This limitation arises from the sputtering process that is the source of ions that are analyzed, and highly dependent on the sample morphology.

SIMS measurements are presented in Paper III, where it is used to detect very low concentrations of nitrogen-containing species in Ag films that are deposited in Ar-N₂ atmosphere.

6. Computer simulations

Computer simulations are used in materials science to better understand the correlation among atomic-scale processes (i.e., processes stipulated by theoretical models) and macroscopic attributes (i.e., experimentally-measured properties). This chapter introduces three computational methods that are used in the present thesis: density functional theory (Section 6.1), *ab initio* molecular dynamics (Section 6.2), and finite-difference time-domain calculations (Section 6.3).

6.1. Density functional theory

Density functional theory (DFT) is a quantum mechanical method used for calculating physical properties of materials, based on their electronic structure. [152] Due to the large number of atoms and electrons in a solid, exact solutions to the Schrödinger equation cannot be found. By reducing the many-body problem to a single-body problem, it becomes possible to find solutions computationally. In DFT, this is achieved using the theorems of Hohenberg and Kohn, [153] which postulate that the total energy of a system is a unique functional of the electron charge density $\rho_{el}(\vec{r})$, and that a minimization of the total energy of the system is obtained for the ground-state of $\rho_{el}(\vec{r})$. The ground state is described by a system of non-interacting electrons in an effective potential field $V_{eff}(\vec{r}) = f(\rho_{el}(\vec{r}))$, which is computed from the attractive nuclear potential and the electronic interaction potential. The single-body Schrödinger equation is then solved in an iterative scheme procedure until convergence of the total energy is achieved.

DFT calculations are performed at temperature 0 K, i.e., molecular and lattice vibrations are not considered, and dynamic phenomena cannot be described. In thin film physics, DFT calculations are primarily used for determining surface formation energies, adsorption energies, and static potential energy landscapes.

DFT calculations are used in Paper I to calculate Ag and Cu adatom adsorption energies, as well as Ag₂ and Cu₂ addimer binding energies on amorphous carbon substrates.

6.2. *Ab initio* molecular dynamics

Molecular dynamics (MD) is a method for calculating the trajectories $\vec{r}(t)$ of particles (e.g., atoms) that interact in gaseous, liquid, or solid phase at finite temperatures (i.e., above 0 K). This is done by solving Newton's equations of motion for the system of interacting particles. In the most common MD approach (also referred to as classical MD), the forces between particles are modelled using

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semi-empirical mathematical models, the interatomic potentials, the choice of which is a key aspect for the physical accuracy of the simulation results. [152]

The utilization of semi-empirical interatomic potentials leads to limitations in MD simulations, e.g., charges appear as static parameters, and atom-connectivity is implicit (i.e., bond breaking and forming cannot be described). [154] *Ab initio* molecular dynamics (AIMD) combines MD simulations with DFT, such that interatomic forces needed for MD are calculated from electronic structure calculations in DFT after each time step. [154,155]

AIMD simulations are performed to study diffusion of Ag and Cu adatoms on amorphous carbon, and determine surface diffusivities as a function of temperature in Paper I.

6.3. Finite-difference time-domain calculations

The finite-difference time-domain (FDTD) method is a computational approach used for solving electrodynamical problems, which discretizes differential equations via approximation with difference equations in the time-domain (as opposed to the frequency-domain). [156] As FDTD is a time-domain technique, it can be used to treat problems in a wide range of frequencies. The calculations are performed by dividing the investigated system into domains and, subsequently, time-integrating the Maxwell's equations (see Eqs. 6.1 and 6.2) on the computational grid [156–158]:

$$\nabla \times \mathbf{E} = -\mu \frac{\delta \mathbf{H}}{\delta t} \quad (6.1)$$

$$\nabla \times \mathbf{H} = \varepsilon_0 \frac{\delta \mathbf{E}}{\delta t} + \frac{\delta \mathbf{P}_0}{\delta t} + \sum_{j=1}^N \frac{\delta \mathbf{P}_j}{\delta t} \quad (6.2)$$

In Eq. 6.1, $\mathbf{E}$ and $\mathbf{H}$ denote the electric and magnetic field, respectively, and μ is the relative permittivity. In Eq. 6.2, ε_0 is the permittivity of free space, and $\mathbf{P}_0$ and $\mathbf{P}_j$ stand for the polarization of the free and bound electrons, respectively.

Expressions for the polarization terms are introduced to Eq. 6.2, in accordance with the treated material system, e.g., $\mathbf{P}_0$ and $\mathbf{P}_j$ can be expressed with help of Drude and Lorentz oscillators, respectively (see Section 5.2.1). Subsequently, Eqs. 6.1 and 6.2 are solved computationally, giving the $\mathbf{E}$ and $\mathbf{H}$ fields at every point in the computational grid in the time domain, from which other optoelectronic properties can be calculated. [157].

FDTD is used in Paper III to calculate the localized surface resonance frequency LSPR of isolated Ag islands on insulating SiO₂ substrates as functions of island size and inter-island spacing.

7. Contribution to the field and outlook

The present thesis focuses on the nanoscale growth dynamics, stress generation, and morphology manipulation of thin metal films on weakly-interacting substrates. My contributions to these topics are outlined in the following.

In **Paper I**, the scaling behavior of characteristic morphological transition thicknesses (i.e., percolation and continuous film formation thickness) during growth of Ag and Cu films on amorphous carbon (a-C) are established as function of deposition rate and temperature. These data are interpreted using a theoretical framework based on the droplet growth theory and the kinetic freezing model for island coalescence, from which the diffusion rates of film forming species during Ag and Cu growth are estimated. By combining experimental data with *ab initio* molecular dynamics simulations, diffusion of multiatomic clusters, rather than monomers, is identified as the rate-limiting structure-forming process during island nucleation.

In **Paper II**, the evolution of stress during Ag and Cu film growth on a-C, and its dependence on growth kinetics (as determined by deposition rate, substrate temperature) are systematically investigated. A general trend toward smaller compressive stress magnitudes with increasing temperature/deposition rate is found, related to increasing grain size/decreasing adatom diffusion length. Exception to this trend is found for Cu films, in which oxygen incorporation from the residual growth atmosphere at low deposition rates inhibits adatom diffusivity and decreases the magnitude of compressive stress.

In **Papers III through V**, the effect of minority metallic and gaseous species (Cu, N₂, O₂) on Ag film morphological evolution on SiO₂ is studied. By employing *in situ* spectroscopic ellipsometry, it is found that addition of minority species at the film growth front promotes 2D morphology, but also yields an increased continuous-layer resistivity. *Ex situ* analyses show that 2D morphology is favored because minority species hinder the rate of coalescence completion. Hence, a novel growth manipulation strategy is devised in which minority species are deployed with high temporal precision to target the initial stages of island nucleation, growth, and coalescence, and thereby achieve 2D morphology, while retaining opto-electronic properties of pure Ag films.

The effect of N₂ on stress type and magnitude in Ag films is studied in **Paper VI**. Ag films grown in N₂-free atmosphere exhibit a typical compressive-tensile-compressive stress evolution as function of thickness, whereby a steady-state stress is reached in the second compressive regime. Addition of N₂ yields (i) onset of island-coalescence—and consequently tensile stress formation—at lower film thicknesses, (ii) higher compressive stress upon continuous film formation, and (iii) a compressive-to-tensile stress transition in the continuous film regime. These stress changes are attributed to strain-energy-minimization driven giant grain growth of grains with soft crystallographic orientation, and film roughening, owing

to decreased surface diffusivity of film-forming species in the presence of nitrogen at the growth front.

The overall results of the thesis provide the foundation to: (i) determine diffusion rates over a wide range of weakly-interacting film/substrate systems; (ii) design non-invasive strategies for morphology manipulation of multifunctional contacts in optoelectronic devices; (iii) complete important missing pieces in the fundamental understanding of stress, which can be used to expand theoretical descriptions for predicting and tuning stress magnitude in thin films.

Research on weakly-interacting film/substrate systems is an emerging topic in the thin film physics community, and it is driven by the increasing demand of components containing such material pairings (e.g., in microelectronics, sensors, etc.). The growth manipulation strategies presented in Papers III through V is a promising concept that can allow a more efficient use of thin films on weakly-interacting substrates such as oxides and van der Waals materials. A next step would be the implementation of these deposition strategies in thin metal film-based applications, where the effects of present gas and metal species on device performance and functionalities need to be further investigated. Although not included in this work, preliminary experiments showed that the presence of minority species with low mobility (e.g., Ti, Cr, Mo) can lead to a delayed continuous film formation in Ag films, implying more pronounced 3D morphology during the island nucleation and growth stage. This effect could be leveraged in the synthesis of nano particles from the vapor phase.

Stress data presented in Paper II is consistent with stress generation models that are widely accepted, stipulating the reversible insertion of adatoms into grain boundaries during film growth. The experimental proof for this mechanism does not exist so far. Only if a conclusive model exists, can *in situ* stress measurements be used to verify the quality of the deposited film, or used for studying new effects, e.g., the stress evolution in films that react chemically during growth.

A specific future research question is related to Paper VI, where tensile stress is formed in Ag films deposited in N₂-containing atmospheres that show giant grain growth, in course of which soft crystallographic orientations overgrow the energetically and kinetically favored (111) oriented grains. Combining *in situ* x-ray diffractometry and substrate curvature measurements in a synchrotron facility would allow unambiguously determine how tensile stress formation and texture selection are connected.

In conclusion, it should be stated that the present work is experimental at its core, and simulations are only used to better understand experimental results and their trends. I expect that further validation of the mechanisms proposed by the present thesis will be obtained in the following years by combining advanced *in situ* and *in operando* imaging and spectroscopic tools with new computational approaches (e.g., artificial intelligence-based simulation tools) that enable atom-by-atom modelling of multicomponent film formation.

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List of appended papers and contributions

Paper I

Atomic-Scale Diffusion Rates during Growth of Thin Metal Films on Weakly-Interacting Substrates.

Jamnig, A.; Sangiovanni, D. G.; Abadías, G.; Sarakinos, K.

Scientific Reports 9 (2019), 6640.

I planned and performed all experimental work (film depositions, *in situ* measurements, *ex situ* film characterization) and analyzed all resulting data. I wrote major parts of the article, and act as corresponding author.

Paper II

The Effect of Kinetics on Intrinsic Stress Generation and Evolution in Sputter-Deposited Films at Conditions of High Atomic Mobility.

Jamnig, A.; Pliatsikas, N.; Sarakinos, K.; Abadías, G.

Journal of Applied Physics 127 (2020), 045302.

I planned and performed the majority of the experimental work (film depositions, *in situ* measurements, *ex situ* film characterization with AFM, XRR) and analyzed all resulting data. I wrote major parts of the article, and act as corresponding author.

Paper III

3D-to-2D Morphology Manipulation of Sputter-Deposited Nanoscale Silver Films on Weakly-Interacting Substrates via Selective Nitrogen Deployment for Multifunctional Metal Contacts.

Jamnig, A.; Pliatsikas, N.; Konpan, M.; Lu, J.; Kehagias, T.; Kotanidis, A. N.; Kalfagiannis, N.; Bellas, D. V.; Lidorikis, E.; Kovač, J.; Abadías, G.; Petrov, I. G.; Greene, J. E.; Sarakinos, K.

ACS Applied Nano Materials 3 (2020), acsanm.0c00736.

I was part of the research strategy development, and performed/supervised experimental work (film depositions, *in situ* measurements, *ex situ* film characterization with XRD, XRR) and analysis of resulting data. I was part of writing the article (introduction, relevant experimental sections, discussion).

Paper IV

Manipulation of thin silver film growth on weakly-interacting silicon dioxide substrates using oxygen as a surfactant.

Pliatsikas, N.; Jamnig, A.; Konpan, M.; Delimitis, A.; Abadías, G.; Sarakinos, K.
Journal of Vacuum Science & Technology A 38 (2020), 043406

I was part of the research strategy development, and supervised experimental work (film depositions, *in situ* measurements, *ex situ* film characterization with XRD, XRR) and analysis of resulting data. I took part in writing the article (introduction, discussion).

Paper V

On the effect of copper on the morphological evolution of thin silver films on weakly-interacting silicon dioxide substrates.

Jamnig, A.; Pliatsikas, N.; A.; Abadías, G.; Sarakinos, K.
(Submitted)

I was part of the research strategy development, and performed experimental work (film depositions, *in situ* measurements, *ex situ* film characterization with XRD, XRR, AFM) and analysis of resulting data. I wrote major parts of the article.

Paper VI

The effect of nitrogen on the stress and morphology evolution during growth of thin silver films.

Jamnig, A.; Pliatsikas, N.; Bahsoun, H.; Sarakinos, K.; Barna, P.; Radnóczy, G.; Abadías, G.
(Manuscript in final preparation)

I developed the research strategy, and performed experimental work (film depositions, *in situ* measurements, *ex situ* film characterization with XRD, XRR, AFM) and analysis of resulting data. I wrote major parts of the article.

List of related but not included work

Paper

Probing the uniformity of silver-doped epitaxial graphene by micro-Raman mapping

Shtepliuk, I.; Ivanov, I. G.; Pliatsikas, N.; Iakimov, T.; Jamnig, A.; Sarakinos, K.; Yakimova, R.

Physica B: Condensed Matter 580 (2020), 411751.

Paper

Interplay between thin silver films and epitaxial graphene

Shtepliuk, I.; Ivanov, I. G.; Pliatsikas, N.; Ben Sedrine, N.; Andersson, O.; Iakimov, T.; Jamnig, A.; Sarakinos, K.; Yakimova, R.

Surface and Coatings Technology 381 (2020), 125200.

Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

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