Nucleation and stress generation in thin films deposited with a pulsed energetic deposition flux

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This thesis presents fundamental mechanisms of nucleation and early growth of and stress generation in thin polycrystalline metal films deposited using pulsed energetic deposition fluxes. The effects of a pulsed deposition flux and energetic bombardment on film nucleation was investigated using in situ stress measurements and in situ ellipsometry to determine the film thickness at which the films become continuous. Ag films where deposited using high power impulse magnetron sputtering (HiPIMS) in two series - one with constant low pulse power to minimize energetic bombardment while varying the pulse frequency and one with a constant pulse frequency while varying the pulse power, resulting in different amounts of energetic bombardment and different deposition rates - to separate the effects of a pulsed deposition flux and energetic bombardment. The thickness at which the film becomes continuous was found to decrease both with increasing pulse frequency and increasing pulse power. The effects of the increased energetic bombardment and deposition rate cannot be separated due to their coupling. Adatom lifetimes and the coalescence times for islands where calculated for different coverages and island sizes and compared to the time between pulses. It was found that the time between pulses was lower than the adatom lifetimes for certain conditions; this leads to an increase in the adatom density and therefore an increase of the nucleation density resulting in smaller thicknesses for the formation of continuous film. It was also found that the coalescence time for clusters becomes longer than the time between pulses, retarding the coalescence process; this leads to formation of long lived elongated clusters also resulting in a decrease of the thickness at which the films become continuous.

Energetic bombardment during growth of Mo films using HiPIMS is found to result in large compressive stresses without the commonly observed defect induced associated lattice expansion seen when depositing films using energetic bombardment. This and a correlation between the magnitude of the compressive stress and the film density allow us to conclude that the compressive stress is generated by grain boundary densification. Two mechanisms leading to grain boundary densification and thus generation of compressive stresses are proposed.
This thesis is part of my PhD studies in the Plasma & Coatings Physics division of the Department of Physics, Chemistry and Biology at Linköping University. The goal of my research is to gain an understanding of the fundamental processes of thin film nucleation and growth using pulsed energetic deposition fluxes. The research is financially supported by the Swedish Research Council.
LIST OF APPENDED PAPERS

Paper 1:  **Time-domain and energetic bombardment effects on the nucleation and post-nucleation characteristics during non-equilibrium film synthesis**

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Manuscript in final preparation

Author’s contribution:
I took a major part in planning the experiments, performed a majority of the depositions and characterization except for the ellipsometry. I took part in the data interpretation and took part in writing the paper.

Paper 2:  **Atomistic mechanisms leading to atom insertion into grain boundaries and compressive stress generation in physical vapor deposited films**

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In manuscript

Author’s contribution:
I took a major part in planning the experiments, performed a majority of the depositions and did all characterization except for the $\sin^2\psi$-measurements. I took part in the data interpretation and took part in writing the paper.
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1. INTRODUCTION

Thin films are material layers with thicknesses ranging from one atomic layer up to several micrometers. They are ubiquitous in the modern world and can be found in such diverse applications as mirrors, eyeglasses, microelectronics, window glass, cutting tools and solar cells. Generally, thin films are used when there is a need to enhance or change the properties of the surface of an object - usually referred to as a substrate - by adding to or changing it’s functionality in some way.

Thin films can be deposited by multiple methods, e.g. form liquids, using for example electrochemistry, or from vapors. Vapor deposition methods are roughly divided in two categories, chemical vapor deposition (CVD) and physical vapor deposition (PVD), although hybrid processes are not unheard of. PVD and CVD processes are differentiated by how material transport and film deposition is facilitated. In CVD processes the deposition material is transported as components of gaseous compounds that are driven to react on the substrate, usually by heating the substrate, leaving a film of the desired material and reactant gases. PVD processes use a solid (or sometimes liquid) materials source that is vaporized, ideally, generating a stream of single atoms that are deposited on the substrate. As atoms deposit on the substrate surface they form nuclei, which as more material is deposited grow, impinge on each other and form a continuous film. These processes are affected by the flux of depositing species, modulation of the deposition flux and the energy of the impinging species as well as conditions on the substrate such as temperature and surface structure. Different growth processes can therefore lead to very different film structures which in turn can result in different properties for films of the same material. The dependence of nucleation and early film growth on the flux of deposited species, temperature and energetic bombardment is well investigated for deposition processes using a continuous deposition flux. However, the effects of a pulsed deposition flux on these processes have previously not been investigated in detail. Instead the majority of investigations have focused on the effects of the energetic bombardment, associated with most pulsed deposition processes, on film growth. A film property closely related to the deposition conditions is the intrinsic stress of the film. It is also very important for other film properties such as hardness, electrical properties and film adhesion. A common reason for film stresses is differences in contraction between the film and the substrate leading to tension or compression of the film upon cooling after deposition at elevated temperatures. More significant is that large stresses also are generated by defects
in the crystal structure of the grains, by atomic interactions between grains as well as by surface effects, all of which are dependent on the deposition conditions. Although some mechanisms leading to stress generation are well established others are still topics for debate. My work consists of two parts. The first part deals with how pulsed deposition flux affects nucleation and the early stages of thin film growth. Using the well-characterized system Ag on amorphous SiO$_2$ we investigated the dependence of the thickness at which the film becomes continuous on pulsing frequency, the deposition rate in the pulse and energetic bombardment using in situ stress measurements and in situ spectroscopic ellipsometry. The second focuses on stress generation in hard metal films grown using a partly ionized deposition flux where a large part of the ions have energies around 50 eV. Energetic bombardment at these energies mainly affects the first few atomic layer of the growing film while enhancing surface diffusion. Combining this with low deposition temperatures freezes the state of the film allowing for the investigation of stress generation mechanisms relying on mobile atomic species.
2. Thin Film Growth

Growing thin films go through several distinct stages, each affecting the resulting film microstructure and hence its physical properties in some, sometimes not reversible, ways. This chapter deals with the different growth stages and the process of surface diffusion, which is important in all growth stages, in chronological order from the perspective of a growing film.

2.1. Adatoms and surface diffusion

When an atom or ion impinges on a surface it starts interacting electronically with the surface at a distance of several Å. It collides with the surface and loses most of its momentum and kinetic energy and lowers its potential energy by adsorbing on the surface. Adatoms see a potential energy landscape defined by the atomic structure and chemistry of the surface where adsorption sites of different depth, or stability, are present. The adatoms diffuse between these adsorption sites in a random walk process with the jump rate, \( \Gamma \) (Eq. 1), determined by the thermal jitters of the adatoms or the attempt frequency, \( \nu \), the diffusion barrier, \( E_d \), and the substrate temperature, \( T \), while \( k_B \) denotes Boltzmann’s constant.

\[
\Gamma = \nu e^{-\frac{E_d}{k_B T}} \quad (1)
\]

Assuming that the diffusion barrier is the same in all directions and that the adsorption sites are separated by a distance, \( a \), one can calculate the surface diffusion coefficient or diffusivity to

\[
D = \frac{1}{4} a^2 \Gamma = \frac{1}{4} a^2 \nu e^{-\frac{E_d}{k_B T}} = D_0 e^{-\frac{E_d}{k_B T}}, \quad (2)
\]

where the factor \( \frac{1}{4} \) in the expression is due to the two dimensional nature of surface diffusion [1]. \( D_0 \) and \( E_d \) are the parameters usually given in experimental investigations of surface diffusion. Since \( D \) has the unit m\(^2\)/s it is therefore evident that the lifetime of an adatom, \( \tau_D \), can be calculated (Eq. 3) by making the assumption that adatoms do not desorb from the substrate by taking the average distance between sites with high binding energies e.g. step edges and islands, \( L_0 \), into account. This assumption is valid if the surface binding energy of an adatom is much larger than the diffusion barrier.

\[
\tau_D = \frac{L_0^2}{4 D} \quad (3)
\]

* The Ångström (Å) is a practical length unit when dealing with atoms and is \( 10^{-10} \) m or 0.1 nm.
The diffusion barrier a result of the atomic structure of the surface and varies between materials as well as between differently terminated surfaces of the same material. Depending on the surface structure there also might be different diffusion barriers in different directions on the surface giving preferred directions for diffusion. Diffusion barriers are also affected by the presence of other adatoms, nuclei, impurities and steps on the surface. The barrier most important to the morphology of growing films is the, at first sight rather counterintuitive, step edge barrier or Ehrlich-Schwöbel barrier, $E_{ES}$, which is an additional diffusion barrier for diffusion down surface steps. A similar barrier also exists for atoms diffusing around kinks on step edges. The cause of the step edge barrier can be viewed, in a much-simplified way, in the light of bond coordination. Figure 1 shows a side-view of adatoms on a surface with a step. Moving from one adsorption site to another requires stretching one bond and contracting another, both actions requiring energy. This energy is the diffusion barrier $E_d$.

![Potential energy profile](image)

Figure 1: Cartoon of bonding for A, an adatom in rest, B a diffusing adatom, C an adatom diffusing over a step edge and D an atom bonded to the step edge in a simple cubic lattice. The curve above show the potential energy profile experienced by an adatom.

Going over the step edge requires stretching and breaking the bonds on the top surface and reforming them at the lower surface when going over the edge. Breaking bonds is an energetically expensive action thus resulting in the large diffusion barrier for intralayer diffusion, $E_{ES}$. From this reasoning it is also evident that atoms at the bottom of the step edge are strongly bound to the step. It should be noted that small changes in the energy barriers results in large changes in the diffusion rates as it is situated in the exponential term of Eq. 1. The step edge barrier is often large compared to the diffusion barrier resulting in very low rates of intralayer diffusion when the temperature is low. Adatoms are therefore trapped on top of surface structures when a step edge barrier is present leading to very different film morphologies than when no step edge barrier is present.
Although surface diffusion is normally seen as a thermally activated process there have been direct measurements of increased diffusivities when the surface is subjected to low energy ion bombardment [2,3]. Signs of increased rates of surface diffusion are also commonly observed in the film morphology of films deposited using low energy ion bombardment (see e.g. [4]). Simulations of the effects of energetic bombardment on surfaces show that the processes leading to the larger surface diffusivities are rather complicated and can take a number of different paths [5–7].

2.2. The initial stages of film growth
Thin film deposition is performed under far from ideal conditions, even the best (and very expensive) substrates have rather large densities of various kinds of surface defects such as vacancies and steps, contaminants are present both in the source material and in the residual gas of the deposition chamber, all while the flux of depositing atoms is large. Adatoms are therefore bound to encounter sites on the substrate where they can be trapped or other adatoms to which they can bind. All these events result in less mobile or immobile clusters of adatoms, nuclei, which form in the first stages of film growth.

2.2.1. Nucleation
Adatoms arriving on a perfectly flat surface in the very initial stages of film growth will diffuse randomly until they either encounter another adatom and form a dimer or desorb from the surface. The dimer will, in turn, either dissolve back to two adatoms or absorb yet another adatom and then either grow further as more atoms attaches or shrink back due to detachment of atoms. However, the latter is unlikely due to the high supersaturation† under process conditions commonly encountered in PVD processes. Clusters consisting of two or more atoms are generally stable [1,8], i.e. likely to gain another atom before an atom is lost, and will on average not decay. The critical cluster size, $i^*$, is therefore said to be 1. This is usually the case during low temperature growth. But there are conditions when the critical cluster size is larger than 1, often at high deposition temperatures [1]. The probability of dimer formation and therefore the nucleation density, $N$, depends on the likelihood of two adatoms encountering each other and rises if the number density of adatoms increases. In other words $N$ is proportional with the deposition flux, $F$. On the other hand the probability of two adatoms encountering instead of finding a larger cluster decreases if they are able to move

A surface is supersaturated when the number density of adatoms is larger than the equilibrium number density of adatoms would be at the same temperature.
longer distances, that is if the diffusivity, $D$, is large. This is also found in atomistic nucleation theory from which the scaling relationship,

$$N = \left(\frac{L}{\alpha}\right)^\chi = \left(\frac{L}{\alpha}\right)^\frac{D}{(\tau D)^{1/3}} = \left(\frac{L}{\alpha}\right)^3 (4)$$

where $\chi$ is called the scaling exponent, can be derived [1].

It has been found theoretically [9] and experimentally [10] that equation 4 no longer holds, under certain conditions, when the flux is pulsed. Instead of having a simple dependence on flux and diffusivity the nucleation density instead depends on the pulsing frequency, $f$, the materials flux pulse width, $t_{ON}$, and the average adatom lifetime, $\tau_D$. When the flux is turned on the adatom density will increase to saturate after a time $\tau_D$, the adatom density will then be stable until the flux is turned off after which the adatom density will decay until there are no adatoms left, $\tau_D$ seconds later, see figure 2. If $f$ is low so the time between pulses is larger than the adatom lifetime, $1/f \gg \tau_D$, it is evident that the nucleation density will be proportional to the steady state adatom density reached during the pulse. This in turn depends on the materials flux in the pulse, $F_{pulse}$. In fact the nucleation behavior will be described by a slightly modified equation 4,

$$N = \left(\frac{F_{pulse}}{d}\right)^\chi. (5)$$

A large frequency, $1/f \ll \tau_D$, will never allow the adatom density to decay between the pulses. The adatom density will saturate and then stay at a steady state value proportional to the average flux, $F$, until deposition is ceased. This corresponds to deposition with a continuous flux described by equation 4.
When the adatom lifetime and the time between pulses if approximately the same, \(1/f \approx \tau_D\), there is not enough time for the adatom density to decay to zero between pulses, on the other hand it will not saturate in one pulse. Instead it will saturate after \(n\) pulses,

\[
n \approx \frac{1}{\delta t_{\text{pulsed}}}, \tag{6}
\]

as calculated by Jensen and Niemeyer [9] with the island density saturating at

\[
N \sim (F_{\text{pulsed}} t_{\text{ON}})^{1/2}. \tag{7}
\]

Note that the island density is not dependent on the diffusivity in equation 7. The effect of pulsing frequency on film nucleation is investigated in some detail in Paper 1.

It is also possible to modify the nucleation behavior of thin films by adding impurities or creating defects on the surface to create extra nucleation sites increasing the nucleation density above the kinetic limit. Durand and co-workers [11] found that the nucleation density of Ni and Mo films deposited on highly oriented pyrolitic graphite (HOPG) can be changed by treating the substrates with different doses (number of incident ions per unit area) of 100 eV Ar\(^+\) ions. The nucleation density of the deposited films was found to scale with the ion dose. A larger nucleation density compared to evaporation onto virgin substrates was also found when depositing films using 100 eV Ni\(^+\) ions as the depositing species. Ions in this energy range have enough energy to affect the first few atomic layers of the substrate creating various kinds of surface defects on the HOPG surface [12], the density of which is directly proportional to the ion dose. These defects acts as nucleation centers for adatoms leading to the observed increases in nucleation density. Exposure to impurities, e.g. from the residual gas, also leads to an increase in the nucleation density [1] although these effects can, to a some extent, be mitigated by choosing appropriate deposition conditions, i.e. high deposition rates at high working pressures to minimize the time each growing layer of the surface is exposed to the residual gas.

2.2.2. Grain growth and coarsening

Several processes take place simultaneously as the nuclei grow and become grains. Atoms, either directly from the vapor or adatoms, continuously attaches to and detaches from the grains with a net positive growth rate for most grains. Let’s first look at what happens to a number of differently sized grains when no deposition takes place. Detachment of an atom from a grain is more probable the smaller the grain is as the binding energy of surface atoms depends on the grain curvature, which is inversely proportional to grain size. Each grain will therefore, at every moment, be surrounded a two dimensional cloud of atoms randomly...
attaching and detaching from the grain as illustrated in figure 3. The density of adatoms in this cloud is the largest close to the grain and decreases with distance from the grain. If a small grain and a large grain are situated near each other there will be an adatom concentration gradient between the grains creating a driving force for diffusion leading to a net flux of atoms from the small grain to the large in a process called Ostwald ripening [13–15].

The crystallographic orientation of the grains is more or less random at the early stages of growth, unless the substrate acts as a crystallographic template. It should however be noted that even amorphous substrates might act as templates in the very initial stages of growth [16]. This initial orientation of the grain might not be energetically favorable with regard to the later structure of the grain and will in that case be restructured as the grain grows larger unless the atoms in the grain are not mobile enough. High energy surface and interface structures will be unfavoured meaning that certain grain orientations and surfaces will be more common than others (in the case of fcc-metals, this means grains with surfaces terminated by (111)-faces) as free energy minimization will lead to higher growth rates for the low energy surfaces [17,18].

2.2.3. Coalescence
As the islands grow larger they will eventually meet. As soon as two islands are close enough to interact they will begin restructuring to minimize their total surface and interface energy. The islands will elastically strain and form a grain boundary [16]. Atoms from the grain surface will diffuse along the grain surface into the region around the grain boundary to minimize the free surface of the grains. Size differences between the grains lead to growth of
one of the grains at the expense of the other as the diffusion processes will accelerate due to larger driving forces as the curvature of the smaller grain increases when the size difference between the grains increases. If differently oriented grains of equal sizes coalesce the grain with the lowest energy orientation will grow at the expense of the other further favoring low energy grain orientations increasing the degree of preferred crystallographic orientation of the film.

2.3. Microstructure evolution during film growth

After coalescence the film fully covers the substrate. The structure evolution of the film is now decided by the ability of the atoms on and in the grains to move across the grain surface and between the grains. This chapter deals with how growth proceeds on the surface of a grain and how kinetics affects the surface morphology before looking closer on the structure evolution of films.

2.3.1. Epitaxial growth

The growth mode, and therefore the surface morphology, during epitaxial growth is decided by the material transport between atomic layers of the film, the interlayer transport, the adatom diffusivity (in other words the growth temperature), the width of atomic terraces and the nucleation density [1].

Step flow growth, figure 5 (a), occurs at high temperatures when the distance between steps is shorter than the average distance between nuclei. Instead of forming new nuclei on the terrace adatoms attach to the step edges resulting in lateral movement of the step edges. Step flow growth is, in principle, possible regardless of step edge barriers as it can proceed through adatom attachment to the ascending step. At lower growth temperatures larger supersaturation will lead to island nucleation on the terraces, as the distance between steps now is longer than...
the average distance between nuclei, resulting in layer-by-layer growth, figure 5 (b). Here the islands will grow and coalesce to almost completely fill the first layer before nucleation of new islands in the second layer takes place. The growth temperature must still be high enough or the step-edge barrier low enough for considerable interlayer transport to take place in order to enable layer-by-layer growth.

The presence of a step edge barrier inhibits interlayer transport making pure layer-by-layer growth impossible. Instead mound formation, figure 5 (c), takes place as new layers continuously nucleate as soon as the top terrace is larger than the average distance between nuclei. At very low temperatures intralayer diffusion is inhibited with adatoms sticking in the lattice site where they land resulting in self-affine growth, figure 5 (d). Both mound formation and self-affine growth give rise to a considerable surface roughening that evolves as the film thickens.

This picture presented above is idealized and rather simplistic. Layer-by-layer-like growth can for example also be induced by deposition conditions leading to nucleation of many islands smaller than the critical size needed for secondary layer nucleation. Something that can be achieved by using very high instantaneous deposition rates [19]. Another way of manipulating the growth mode is through energetic bombardment during growth which can be used to
induce interlayer transport also giving rise to layer-by-layer like growth even in the presence of step edge barriers [6,7].

### 2.3.2. Polycrystalline thin films
The microstructure evolution of thin films during growth after coalescence is highly dependent on the deposition conditions. However, already in the early years of thin film deposition some trends crystallized, materials deposited at temperatures above and below certain temperature thresholds in comparison to their melting temperatures displayed similar microstructures, see for example [4,16,20,21] and references therein. This gave rise to the widely used structure zone diagrams, two example of which is shown in figure 6, where the microstructure evolution is shown schematically as a function of the homologous temperature, or the substrate temperature normalized to the melting temperature ($T_s/T_m$) of the deposited material, and the energy of the depositing species. Films deposited at substrate temperatures far from their melting temperature ($T_s/T_m < 0.3$) usually consist of fibrous columnar grains with voided grain boundaries while films deposited at higher temperatures ($0.5 < T_s/T_m < 0.8$) consist of large columnar grains with dense grain boundaries. At temperatures close to the melting point ($T_s/T_m > 0.8$) films consist of large equiaxed grains forming due to recrystallization and segregation of impurities to the surface and grain boundaries. These growth regimes are called zone I, II and III in order of rising temperature. Films deposited by e.g. sputter deposition also have an additional dependence on energy transferred from energetic particles to the film, which can be varied by varying the process pressure or by attracting ions to the substrate using a substrate bias, giving rise to an additional zone between zone I and II called zone T. The temperature range where zone T occurs varies with the energy and flux of the bombarding particles. It should be noted that some of the structure zone models where developed for comparatively thick films, at several hundred micrometers.
Some of the development with film thickness may not occur for thin films especially when deposition is performed using high purity materials under clean deposition condition, zone III growth is therefore usually not observed in thin films.

The distinct zones occur because of the difference in activation energy for different diffusion processes. At the low temperatures of zone I even surface diffusion with its rather low activation energy is slow, thus deposited atoms stick more or less where they land leading to large nucleation densities and grains with a small lateral footprint. The growth mode on top of the grains will be self-affine leading to surface roughness build-up causing shadowing around the grain boundaries causing the voided grain boundaries. Increasing the surface diffusivity, induced by higher temperature and/or energetic bombardment of the growing film, leads to gradual changes of the structure. The grains grow slightly larger, the grain surface smoother and the grain boundaries denser. Going from a low energy deposition flux to a high energy (here up to some hundreds of eV) flux at a constant growth temperature also induces microstructural changes as illustrated in figure 6 b. Low energy bombardment only affects the surface layers leading to enhanced adatom diffusion, higher energy bombardment (some tens of eV depending on the material) lead to defect creation first few layers of the film which might act as nucleation sites and can lead to renucleation. Yet larger bombarding energies lead to the creation of more defects making renucleation more common resulting in equiaxed nanocrystalline films [4,22].

When the diffusivity is large enough for adatoms to cross the grain boundaries competitive growth comes into play and the film structure evolution is characterized by zone T growth. The temperatures at which zone T growth occurs are not high enough to give rise to any preferred crystallographic orientation during nucleation and grain growth, the grains are therefore randomly oriented at the initial growth stages. Depositing atoms therefore land on different surfaces with varying adatom diffusivities. Adatoms on high mobility surfaces will diffuse larger distances before settling than adatoms on low mobility surfaces and will, if they are close to a grain boundary, have a larger likelihood of jumping to a neighboring grain. This results in a net flux of atoms from grains terminated by high mobility surfaces to grains terminated by low mobility surfaces and therefore a higher growth rate for these grains. These grains are also more prone to have a mound-like growth mode leading a buildup of surface roughness causing shadowing and a yet higher different in growth rate for different grains. The shadowing also leads to less deposition near the grain boundaries and development of grain boundary porosity. The grains where adatom mobility is the lowest will overgrow
the grains terminated by high mobility surfaces leading to films with a strong preferred crystallographic orientation and a lateral grain size and surface roughness that increase with film thickness.

Zone II growth takes place at temperatures when bulk diffusion becomes significant. Grain boundaries are mobile throughout the growth process as well as post deposition. Grain growth minimizing the grain boundary and surface areas therefore takes place not only during the initial growth stages but also during growth of a continuous film. This process, known as continuous or normal grain growth where all growing grains have approximately the same grain size, stops only when the grains have a strong preferred orientation or when the lateral grain size reaches 2 to 3 times the film thickness [4]. Grain growth can continue via discontinuous, or abnormal, growth where only a subset of all grains grows to very large sizes. The growing grains must have a considerable energetic advantage over the neighboring grains for discontinuous grain growth to take place.

2.4. Intrinsic stresses in thin films

Large mechanical stresses can be generated in thin films causing adhesion problem and substrate bending as well as affecting the mechanical, optical and electrical properties of the films [23]. These stresses are divided into extrinsic stresses arising from external influences and intrinsic stresses generated in the film. The most commonly mentioned extrinsic stress being stress generated upon heating a film-substrate system with different thermal expansion coefficients although wear or bending of the substrate also gives rise to considerable stresses in the film. Intrinsic stresses are generated in the film and are closely related to the microstructure evolution, crystallographic defects and growth process of the film. Film stress can be measured by two principal methods, through X-ray diffraction [24] and substrate curvature measurements [25]. X-ray diffraction measures the crystallographic strain

\[ \varepsilon = \frac{d_d - d_o}{d_o} \]

where \( d \) is the measured lattice spacing and \( d_o \) is the strain free lattice spacing. The film stress, \( \sigma \), is then related to the strain through

\[ \sigma = Y\varepsilon \]

where \( Y \) is the Young’s modulus of the film material. Substrate curvature methods provide a direct measure of the total stress, \( \sigma \), in the film. The methods used to measure film stresses in this work are treated in more detail in 4.1.1 and 4.2.
Early *in situ* measurements [26], also confirmed lately [27], of the film stress during growth of Ag films revealed an evolution of the film stresses with increasing film thickness. The stress was compressive during early growth then switched sign and became tensile just to switch sign again and become compressive. At the late stages of growth the film stress switched sign one again to become tensile. Microstructural investigations have shown that the compressive-to-tensile and tensile-to-compressive [26–28] stress transitions, figure 7, took place at the film thickness corresponding to the onset of coalescence and at the formation of a continuous film respectively. Later experiments [29–31] showed that the late compressive-to-tensile transition disappeared when the background pressure used during deposition was reduced, this transition was therefore attributed to contamination of the film. Deposition interruptions results in reversible stress relaxations, figure 8 b, to a more tensile stress state at all stages of the stress evolution [32,33] while long post deposition relaxation experiments [34,35] have shown that these relaxation processes continues for at least 20 h. Other experiments [36] have shown that the magnitude of the stress relaxation is inversely proportional to the grain size in the film. Growth of low mobility materials results in a different stress evolution [37,38]. In the initial growth stages the film stress develops as in high mobility materials, the similarities stop after coalescence [23]. Here the film stress is generally tensile but can exhibit gradients in the stress magnitude. Stress relaxations are usually not observed upon growth interruptions.

The initial compressive stress is observed during the nucleation and growth of separated islands. At these size scales, with grain diameters below 10 nm, surface effects are of great
importance for many materials properties, so also in the case of film stresses. Surface atoms are coordinated differently than atoms in the bulk of the material leading to driving forces for different lattice spacings in the surface layer, and sometimes to reconstructions of the atomic structure of the surface, in order to accommodate the free bonds. This drive to change the lattice spacing at the surface cannot be fully accommodated as the surface atoms still must remain in positions close to those dictated by the bulk lattice. The surface atoms therefore experience a force acting along the surface to hold them in place, referred to as the surface stress [39–41]. The surface stress gives rise to pressure, called the Laplace pressure, which is inversely proportional to the radius of the body of material. Small crystallites therefore experiences large Laplace pressures resulting in a large compressive strain in the crystallite and a smaller equilibrium lattice parameter. Growing islands will therefore see a change in the equilibrium lattice parameter to values closer to the bulk value with increasing size. However, the lattice parameter will only be able to change when the island is mobile as the atoms in the substrate-island interface otherwise are fixed. Growth on the island will proceed through epitaxy giving rise to strain in the island as the lattice parameter will vary with the height in the island. The build-up of strain in the growing islands results in a compressive biaxial stress in the film that will continue to build up until the onset of coalescence.

The generation of tensile stress in the early stages of film growth is as we have seen closely connected to island coalescence. When islands coalesce they, as previously mentioned in 2.2.3, elastically deform [16,42–44] to form grain boundaries as in order to decrease to the their free energy by decreasing the surface energy. The deformation of the islands will result in a change in the strain state in the islands from compressive to tensile and therefore also result in a build-up of tensile film stress until the completion of coalescence.

A number of mechanisms have been suggested to explain the stress evolution after coalescence in high and low mobility materials, especially the compressive stresses in high mobility materials have been subject to controversial debate in the last decade. Resolution of these issues is complicated by the dynamic nature of the stress evolution that makes post deposition structural characterization almost impossible as the stress will relax before or during any measurements. Cammarata and co-workers [40] have suggested that the film inherit the compressive stress generated before coalescence as the tensile stresses generated during coalescence will not be able to relieve the compressive stress in large grained films. The compressive stress generated in the pre-coalescence stage would then propagate in the film through the epitaxial growth of the grains. Other suggested mechanisms involve surface
stresses. The surface structure of growing films is continuously changing as new islands nucleate and grow on top the old surface layers. This gives rise to a larger step edge density which locally will result in a change of the surface stress [41]. This mechanism also provides an elegant explanation for the stress relaxations observed at growth interruptions as the step edge density will decrease through surface diffusion when the deposition flux is turned off. Adatoms and other surface defects should also give rise to local changes in the surface stress and the stress state of the film. This has also been suggested by Friesen and co-workers [45] after experiments where the stress evolution of epitaxially grown Cu(111) have been measured simultaneously with reflection high energy electron diffraction (RHEED) measurements performed to characterize the surface defect evolution showing that the surface defect density and the film stress was correlated. The same authors later extended this argument to polycrystalline films [33]. The surface defect density will decrease upon growth interruptions as the surface defects are mobile which result in a stress relaxation upon growth interrupts. Chason and co-workers [46] suggested adatom insertion into grain boundaries as a source of compressive stress. During deposition the chemical potential of the surface will be larger than during equilibrium conditions while the chemical potential of the grain boundaries will be lower than that of the surface due to their underdense nature. This difference results in a driving force for diffusion into the grain boundaries and insertion of adatoms into the grain boundaries. These atoms take misfitting positions in relation to the lattice in the grains leading to repulsive forces over the grain boundary and compressive stress in the grains. When growth is interrupted the driving force is reversed leading to out diffusion of the misfitting atoms and a stress relaxation. This model assumes very large grain boundary mobility and the possibility for atoms to diffuse freely along the full length of the grain boundary, an assumption that in most cases is unphysical. This shortcoming has been addressed recently [47] in a reworked model based on adatom incorporation into grain boundaries that does not require grain boundary diffusion. Instead the model assumes that adatoms are incorporated at the top of the grain boundary and locked in as the grain boundary height increases on further growth. A consequence of Chason’s model is that the magnitude of both the steady state compressive stress and the stress relaxation should be inversely proportional to the grain boundary length which was shown to be the case by Leib et al. [36]. Another consequence is that compressive stress generation and relaxation should be kinetically limited processes exhibiting temperature dependences. This is true for stress generation, see for example Koch [35], but it does not seem to be the case for stress relaxations [34].
Experimental determination of which of the proposed mechanisms are valid is difficult as they all manifest in very similar ways. In some cases the magnitudes of the stresses generated can be estimated in computer simulations. This way it has been shown that surface defect induced stress does not reach the magnitude needed to fully explain the measured compressive stress during growth [48] while other simulations [49,50] have shown that insertion of adatoms into the grain boundary seems to account for a most of the generated stress.

![Figure 8](image.png)

**Figure 8:** a) Stress evolution of Mo deposited on SiO$_2$ without substrate heating resulting in a tensile stress state of the film. b) The stress evolution of Ag deposited on SiO$_2$ as a function of time. Observe the reversible stress relaxations occurring on deposition interruptions for Ag but not for Mo (shaded areas).

When lowering the homologous temperature at deposition the stress evolution changes from the compressive-tensile-compressive evolution observed at high homologous temperature to a compressive-tensile evolution [35] where no stress relaxation takes place at deposition interruptions, figure 8 (a). It is common that the magnitude of the tensile stress is not constant during deposition but decreases with increasing film thickness [51]. By depositing films to different thicknesses and then etching back a thick film to the same thicknesses and measuring the film stress at each point it has been shown [51] that no stress relaxation takes place but rather that a stress gradient is present in the film. It was also observed that the magnitude of the film stress was inversely proportional to the grain size leading to the conclusion that the tensile stress in low mobility materials is generated but attraction between grains over grain boundaries as had been suggested by Hoffmann [52]. Low energy ion bombardment (with ion energies above approximately 50 eV depending on the film material) of the growing films usually results in compressive film stresses and, if the bombarding energy is chosen carefully, similar underdense microstructures as films deposited without energetic bombardment. Comparing two such films Janssen and co-workers [53] found that
the change in stress magnitude between the films does not vary with film thickness, and hence grain size, which implies that compressive stress induced by ion bombardment is not generated in the grain boundaries. Additionally they found that the results from \( \sin^2 \psi \)-measurements of compressively stressed films deviates from the behavior expected when the films are biaxially stressed, instead they are in a triaxial stress state. In other words instead of the grains being squeezed between expanding grain boundaries they found that the crystal lattice of the grains inflates. This is in agreement with other investigations at deposition conditions leading to compressive film stresses \([54–57]\) and shows that lattice defects induced by the energetic bombardment is the cause of the compressive stress. The observed stress gradients are therefore not due to a stress relaxation but is caused by the constant defect induced stress in the grains being additive with the tensile stress generated in the grain boundaries which is dependent on the grain size. Compressive stresses generated in the grain boundaries are not as commonly seen under conditions with low adatom mobility, they have however been observed by decoupling the stress components generated by measuring the film stresses in ZrN films using both the \( \sin^2 \psi \)-method and the wafer curvature method as these provide information about the stress state in the crystalline regions of the film and the whole film respectively \([58]\). From this it was observed that the stress generated in the grain boundaries was compressive for films deposited at low pressures and tensile for films deposited at high pressures. Films deposited at low pressures are subjected to higher energies of bombarding particles, from both sputtered and backscattered particles, due to a lower probability of collisions in the gas phase, resulting in dense films with a smooth surface.
In Paper 2 we find that Mo films deposited under a high flux of low energy Mo- and Ar-ion bombardment are compressively stressed with the stress magnitude being dependent on the energy and flux of the bombardment. Measurements showed that the stress free lattice parameter was only slightly expanded (< 0.2 %) in comparison to the bulk value and that the expansion was independent of the energy and flux of the bombarding species. This shows that the film stress is predominantly biaxial and that the defect induced lattice expansion is not the main cause of the compressive stress in these films. The stress must instead be generated in the grain boundaries. The magnitude of the film stress is correlated with a high film densities and smooth film surfaces. Partly building on Chason’s model of stress generation [46,47] we suggest the following mechanism for stress generation, illustrated in figure 9. The large fraction of energetic deposition species generated by high power impulse magnetron sputtering (HiPIMS) discharges (see 3.3) lead to large intra- and interlayer diffusivities [7,59] and implantation of depositing species into the first few atomic layers of the growing film. In the vicinity of the grain boundary this leads to a step-flow-like growth mode where steps are able to migrate until they meet the also-migrating steps of the opposite side of the grain boundary resulting in dense grain boundaries. Energetic species implanted into the first few atomic layers lead to creation of both metal and gas interstitials. Single metal interstitials are

Figure 9: Schematic image of the suggested mechanisms for insertion of atoms into grain boundaries. Energetic deposition species are shallowly implanted (the dashed grey lines mark the maximum implantation depth). Metal atoms are shown as black circles, inert gas atoms as grey circles. Bulk interstitials give rise to hydrostatic stresses (short arrows). The area where atom diffusion into the grain boundary is enhanced is shaded grey.
usually not stable in metals unless they can form clusters [60] and will experience a driving force for diffusion towards the closest underdense region, either the surface or a grain boundary. The energy required for interstitial diffusion is continuously supplied to the surface layers by bombarding species. The enhanced diffusivities make it possible for atoms deposited away from the grain boundary to diffuse into the top of the grain boundary to reduce their free energy. Depositing species can also be directly implanted into the grain boundary. However, this requires the depositing specie to hit a very small region, a process that is a lot less likely than insertion by surface diffusion or interstitial diffusion as both these processes have catchment regions that are several unit cells wide.
3. DEPOSITION PROCESSES

Thin films are deposited by a number of physical vapor deposition (PVD) processes. Most deposition processes are performed under vacuum, usually at background pressures between $10^{-12}$-$10^{-6}$ Torr, in order to minimize contamination of the growing film. Among the least complicated are various evaporation processes where the deposition material is heated by resistive or electron beam heating so that atoms start evaporating. The evaporated atoms have a kinetic energy of ~0.2 eV, which as mentioned in previous chapters might be less than what is required to achieve a desired film morphology. The depositing species are more energetic, ~3 eV, when generated by the plasma based sputtering process. In sputtering energetic bombardment can also easily be achieved by applying a negative voltage on the substrate to attract working gas ions. Both evaporation and sputtering generates a deposition flux consisting predominantly of neutral species making them line-of-sight deposition methods where the directionality of the deposition flux cannot be controlled easily. A desire for larger levels of control of the energy and directionality of the deposition flux resulting in more uniform film thicknesses on substrates with complex shapes have driven the development of ionized PVD processes, examples of which are pulsed laser deposition, arc evaporation and a variety of ionized sputtering processes. The common denominator of all these processes is that utilize high density plasmas to ionize the depositing species either through applying high power densities to very small areas as in pulsed laser deposition, arc evaporation or high power impulse magnetron sputtering or by using secondary plasma discharges, for example RF-coils or microwave discharges, in conjunction with a sputtering source. The deposition processes magnetron sputtering and high power impulse magnetron sputtering used in this thesis will be treated in more detail after a short review of some basic plasma physics.

3.1. Basic plasma physics

A plasma is a quasi-neutral gas-like state of matter consisting of neutral atoms an approximately equal numbers of ions and electrons that can be produced by heating a gas to a high enough temperature [20,61]. Outer shell electrons will then free themselves from the gas atoms creating free electrons and ions, the resulting plasma is a so-called thermal plasma.
where the electrons, ions and neutrals have the same temperature\(^1\). Thermal plasmas are impractical from a processing perspective as the temperatures needed to create the plasma are high, on the order of tens of thousands K which will cause damage to or destroy the objects meant to be treated. In processing, such as thin film deposition, it is therefore more common to use non-equilibrium plasmas, where electrons are much more energetic than ions, sustained by energizing the electrons using powered electrodes. The difference in ion and electron energies originates in the low ionized fraction of the gas, usually below 10\%, in these plasmas. Energetic gas ions are likely to collide with thermal gas atoms loosing much of their kinetic energy in the process. The low number of ions and therefore collisions means that the gas temperature will not be affected by this heating leaving the ion and the gas temperature close to room temperature, with the kinetic energy of gas species being 0.025 eV. The electrons on the other hand have a wide energy distribution ranging from 1-10 eV and sometimes more and hence very high temperatures.

\[ U (V) \]

\[ \text{Plasma potential} \]

\[ 0 \]

\[ \text{Anode} \]

\[ \text{Floating potential} \]

\[ \text{Sheath} \]

\[ \text{Cathode voltage} \]

\[ L (m) \]

**Figure 10: The potential profile in a plasma. The dashed lines mark the sheath edges.**

Because of their much lower mass electrons are more mobile than ions. For plasmas contained in a conducting vessel, such as a metal vacuum chamber, this results in a larger flux of electrons escaping the plasma volume to the chamber wall. The escaping electrons will

\(^1\) In plasma physics temperature is often used as a measure of the kinetic energy of particles. A kinetic energy of 1 eV corresponds to a temperature of \(-11600\) K.
result in a positive potential in the plasma bulk making it more difficult for electrons to escape the plasma. This potential, called the plasma potential, will increase until an equal number of electrons and ions escape the plasma thus maintaining the overall neutrality of the plasma. The plasma potential is usually a few volts above zero, figure 10, resulting in an acceleration of the ions escaping the plasma towards the chamber wall to a kinetic energy of the same order. When an electrically floating object is inserted into the plasma it will, again due to the electron mobility being larger than the ion mobility, be subjected to an electron flux that is larger than the ion flux leading to the build-up of negative charge on the object. The charge build-up will balance when the negative potential of the object is large enough to repel enough electrons to balance the electron and ion fluxes. This steady state potential is called the floating potential. The regions between the electrodes and the plasma where a majority of the potential drop between the plasma potential and the electrode potential takes place are called the plasma sheaths. Electrons generated in the sheaths are accelerated into the plasma due to the large electric fields across the sheaths. Electrons generated at the cathode in an electrically driven plasma are accelerated to the full potential drop of the plasma sheath. In the plasma there is a high likelihood of collisions between an electron and an atom or ion. Elastic collisions result in little energy transfer between electrons and atoms due to the large mass difference resulting in little more than changes of the electron trajectories due to scattering. Inelastic collisions between electrons and atoms might however result in direct ionization of the atom through the process

$$e^- + A \rightarrow A^+ + 2e^-, (10)$$

known as electron impact ionization. Inelastic collisions can also result in excitation of the atom

$$e^- + A \rightarrow A^* + e^-. (10)$$

The excited species provide the visible manifestation of the plasma through light emission at their characteristic wavelengths when the electrons decay to lower energy states. Excited species can also take part in ionization by transferring the excitation energy to another atom instead of emitting a photon

$$A^* + B \rightarrow A + B^+ (11)$$
in a process known as Penning ionization. Atoms can also be ionized in charge exchange collisions where an electron is transferred from an atom to an ion

$$A^+ + B \rightarrow A + B^+. (12)$$
The relative probabilities of these processes are dependent on the number density of the respective species, their energies and the energy required for ionization of an atom. The densities and energies of the species are in turn affected by gas pressure, gas composition and discharge conditions.

The plasma used in sputtering processes is usually generated by applying a negative voltage of a few hundred volts to the target, or cathode, when it is kept in an inert gas, usually Ar, environment at a low pressure contained in a vacuum vessel. Free electrons§ are then accelerated between towards the anode of the system, most often the chamber walls, by the potential difference between cathode and anode. If the gas pressure is high enough the mean free path for collisions between the electrons and the gas atoms will be low enough for the electrons to collide with one or several atoms. Some of these collisions will result in ionization of the gas atoms and the generation of more free electrons. This will lead to an avalanching number of ionizing collisions and the creation of a sustained plasma if the number of electrons produced through ionizing collisions is the same as or larger than the number of electrons being lost to the anode. The ions created in the initial ionization events will be accelerated towards the cathode by the electric field, while when the plasma has ignited any ions reaching the plasma sheath will be accelerated towards the cathode. Ions colliding with the target can cause sputtering and secondary electron emission. Secondary electrons are emitted in an Auger-like process when an incoming ion is neutralized by an electron from the surface resulting in a release of energy. Most often this energy is emitted as a photon but sometimes the energy can be transferred to another electron providing it with enough energy to escape the surface. The secondary electrons are then accelerated through the plasma sheath into the plasma causing the additional ionizing collisions necessary to sustain the plasma.

3.2. Magnetron sputtering

Sputtering is the ejection of atoms from a materials source, or target, after impact of an energetic atom or ion. These ions are often extracted from the plasma in front of the target, although it is also possible to use for example ion beams for sputtering. The ions will be neutralized just above the surface and collide with target atoms transferring their momentum to the target atoms generating collision cascades in the target. Some of the momentum in the collision cascades will be directed towards the surface and can result in the ejection of an

§ There are always some free electrons in a gas generated in ionizing collisions with for example cosmic rays.
atom if the kinetic energy transferred to the atom is larger than the surface binding energy of target material. Two of the advantages of sputtering compared to evaporation are that any material can be sputtered and that sputtering provides a hyperthermal deposition flux. Sputtered atoms initially have a broad energy distribution with a most common energy close to the surface binding energy of the target material, a few eV for most metals, but are slowed down by collisions in the gas phase and are eventually thermalized if the working pressure or the distance travelled is high. Sputter gas atoms can also be backscattered from elastic collisions with target atoms. The energy of backscattered species and the probability of backscattering increase with increasing atomic mass of the target atoms. For heavier elements sputtered with Ar the energy of backscattered species can reach a few hundred eV. For example the energy of backscattered Ar atoms in sputtering of Ag and Mo (both have a mass of ~100 amu) calculated assuming elastic collisions is about 40% of the incident ion energy, which is approximately equal to the cathode voltage. Figure 11 (a) shows the initial energy of backscattered Ar atoms with an incidence energy of 774 eV backscattered from an Mo target determined by the SRIM software [62] and (b) shows the energy of the backscattered species after transport in the gas to the substrate 7.5 cm from the cathode at a pressure of 1.25 mTorr as determined by the SIMTRA software [63].

In early sputter deposition systems pressures on the order of 100 mTorr and voltages up to several kV were needed to provide enough ionization events to sustain the plasma. At these pressures the mean free path of collision for a sputtered atom is below one millimeter resulting in thermalization of the sputtered species well before they impinge on the substrate, usually placed several cm from the target, which is undesirable from a film growth point of
Desirable working pressures for sputter deposition are usually 1-20 mTorr. A way of increasing the number of collisions for the electrons at low pressures is to increase the path length they travel before reaching the chamber wall. This can be done by confining the electrons in a magnetic field. Electrons at a velocity, \( v \), in an electric field, \( E \), and a magnetic field, \( B \), will experience a Lorentz force,

\[
F = q(E + v \times B).
\] (13)

Sputtering magnetrons makes use of this by trapping electrons in a magnetic trap consisting of two concentric magnets of opposite polarity that are placed behind the target forming a doughnut shaped magnetic trap in front of the target, figure. The electric and magnetic fields will be parallel close to the target surface forcing secondary electrons emitted in a direction non-parallel to the electric and magnetic fields to move in a gyrating motion around the field lines trapping the electrons within the magnetic trap. The magnetic field strength is chosen so that the electron gyration radius is on the order of millimeters while still not affecting the motion of the ions to a large extent. Introduction of a magnetron drastically increases the path travelled by electrons thus increasing the number of ionizing collisions per secondary electron reducing the practical operating pressure for a sputtering discharge to below one mTorr. If the field strength of the inner and outer magnets is the same most electrons will not be able to escape the magnetic trap confining the plasma close to the target, figure 12 (a). This is usually not desired as some plasma in the vicinity of the substrate can be utilized to provide large fluxes of ions for controlled energetic bombardment by application of a voltage to the substrate. The magnetic trap formed by a magnetron can be made to leak electrons and thus extend the plasma towards the substrate by having different magnetic field strengths on the

![Figure 12: Two magnetron configurations: a) balanced magnetron b) unbalanced magnetron. The grey regions show the extent of the region of the plasma with the highest density.](image-url)
inner and outer magnets. If the inner magnet is stronger than the outer magnet the trap will leak electrons sideways. While, when the outer magnet is stronger the plasma be able to extend in front of the target, figure 12 (b).

Although energetic bombardment using working gas ions is an effective way to modify growing films it is sometimes desirable to have an ionized deposition flux. This partly alleviates the line of sight character of the neutral dominated deposition flux of magnetron sputtering to some extent allowing for deposition of uniform films on non-flat substrates as ionized species are steered by the electric fields in the plasma sheaths surrounding all objects immersed in a plasma to impinge at angles close to the substrate normal [64]. The dominating ionization mechanism in magnetron sputtering discharges is Penning ionization [61] due to the low plasma density (~10^{16} m^{-3}). The low probability of collision between an excited gas atom and a sputtered atom results in a low ionization of the sputtered flux. A more efficient route to ionize the sputtered material is electron impact ionization, which is promoted by increasing the plasma density and/or the electron temperature. The desire to ionize the sputtered flux has lead to the development of a number of modifications to magnetron sputtering where the magnetron discharge is complemented by additional plasma sources, for example RF-coils or microwave cavities [65], used to enhance the plasma density thus leading to ionization of the sputtered species.

3.3. High power impulse magnetron sputtering

Another way of realizing an ionized deposition flux is to apply a very high power to the target thus increasing the plasma density in a normal sputtering discharge. The high heat load on the target quickly makes a continuous process impossible. If instead the power is applied in short

Figure 13: Examples of HiPIMS pulses during sputtering of Ag at a) low pulse power and b) high pulse power.

27
pulses with a low duty cycle it is possible to keep the average power at the same level a
continuous sputtering discharge while applying powers several orders of magnitude higher in
the pulses. In high power impulse magnetron sputtering (HiPIMS) discharges the pulse on-
time is usually 10 - 500 µs while the pulsing frequency ranges from 10 Hz - 10 kHz with peak
power and current densities of up to tens of kW/cm² and tens of A/cm² respectively [65–67].
Two examples of HiPIMS pulses can be seen in figure 12. The high power densities result in
plasma densities up to $10^{19}$ m$^{-3}$ [68,69] and ionized fractions of up to 90% of the sputtered
material for some materials [70]. Both singly and doubly charged metal ions are usually
observed but metal ions in higher charge states can also be generated for some discharge
conditions [71]. The ionized sputtered species are more energetic than sputtered neutrals
exhibiting a broad ion energy distribution with a tail extending out to ~100 eV. The sputtered
ion population consists of two subpopulations that can be resolved in time-resolved mass
spectrometry measurements, figure 13. A large population having a wide energy distribution
centered around ~40 eV in figure 13, this number is highly dependent on operating pressure,
and a high energy tail arriving to the spectrometer during the first few hundred microseconds
after the pulse and a nearly thermalized population declining with time arriving after the
ergetic ions. The highly ionized flux is also the cause of the main disadvantages of HiPIMS
compared to ordinary magnetron sputtering. If the sputtered species are ionized close enough
to the target only the most energetic ions will be able to escape the potential well of the
plasma sheath, other ions will be back attracted to the target and take part in the sputtering
process. The self-sputter yield of metals is usually much lower than the sputter yield for Ar
resulting in a loss of deposition rate of varying severity. Losses of a few percent up to 70%,
depending on target material and HiPIMS parameters, compared to magnetron sputtering at
similar discharge powers have been reported [65–67,72,73]. The prevalence of energetic
multiply charged metal ions can result in bombardment induced growth defects affecting the
physical properties of the film. These effects are especially severe if a negative bias voltage is
applied to the substrate as these multiply charged ions are accelerated by their charge number
times any potential drop they experience [74].
The effects of the highly ionized and energetic flux on growing films have been investigated for a number of material systems. Films deposited using HiPIMS generally have a dense microstructure and smooth surfaces even when deposited without intentional substrate heating [22,75,76]. This is connected to the intrinsic energetic bombardment in the process and could be the result of the mechanism we suggest in Paper 2, also described in 2.4, that connects grain boundary densification and large compressive stresses generated in the grain boundaries. If the bombarding ion flux and ion energy are large enough they might cause re-nucleation on top of the growing grains resulting in a nanocrystalline film morphology [22]. Energetic bombardment is also important in phase formation where high temperature phases like $\alpha$-Ta [77], the anatase and/or rutile phases of TiO$_2$ [78,79] and $\alpha$-Al$_2$O$_3$ [80,81] which can be formed at comparatively temperatures when the impinging ion energy and flux have been tuned by varying the pulse parameters of the HiPIMS discharge.

Figure 14: A time-resolved measurement of the ion energy distribution function of Mo$^+$ ions in a HiPIMS discharge at a working pressure of 1.25 mTorr. The peak energy is highly dependent on the working pressure and shifts to lower energies at higher pressures due to scattering on gas species.
4. Thin Film Characterization

The structural and mechanical properties of thin films can be probed by a wide variety of techniques. This chapter introduces the techniques and methods used in the work connected to this thesis.

4.1. X-ray diffraction

X-ray diffraction is one of the most useful characterization methods as it can provide a great deal of information about the film without requiring much sample preparation [82]. The method relies on constructive and destructive interference of a collimated and ideally monochromatic X-ray beam in the atomic planes of the sample. Constructive interference will occur when the Bragg criterion

$$2d \sin(\theta) = n\lambda, \quad (14)$$

is fulfilled, here $d$ is the lattice spacing of the crystal, $\lambda$ the wavelength of the X-rays, $\theta$ the scattering angle and $n$ an integer. That is, constructive interference will occur when the path difference for X-rays reflected in parallel atomic planes is a whole number of wavelengths.

![Figure 15: The geometry of the Bragg criterion. The path difference between two waves reflected in different atomic layers, $2d \sin\theta$, need to be an even number of wavelengths for constructive interference to occur.](image)

Measuring the intensity of X-rays scattered in the sample as a function of the scattering angle will give rise to peaks in the spectrum corresponding to the lattice spacings of the different atomic planes fulfilling the Bragg criterion. X-ray diffraction can be used to find the crystalline quality and the orientation of the crystallites of a sample. It can also be used to determine the film thickness, crystallite sizes and in some cases the chemical composition and chemical modulation of the sample.
XRD line scans are most often performed in two different geometries. The θ-2θ-scan where the incidence angle, θ, and the scattering angle, 2θ, are scanned synchronously. In this mode scattering only takes place in lattice planes parallel with the sample surface. By comparing the peak intensities from the different lattice planes in θ-2θ-scans it is possible to approximate the degree of preferred orientation of the grains in the film by comparing the peak intensities. In the grazing incidence geometry the incidence angle is kept constant at a small angle, usually below 5 degrees, while the scattering angle is varied. The small incidence angle results the X-rays travelling a longer path through the film resulting in more scattered intensity from the film. Due to the geometry scattering takes place in lattice planes of different grains for all scattering angles. The results can therefore not be used to gauge the degree of preferred orientation and might miss peaks entirely if the film crystallites are highly aligned.

Changes in the lattice spacing in the film crystallites will manifest as shifts of the diffraction peak compared to the unstrained peak position, if the lattice expands or contracts equally everywhere in the film, or peak broadening, if there is a distribution of lattice spacings. In-plane film stress, intrinsic or extrinsic, results in an out-of-plane expansion or contraction of the lattice, and thus shifts of the diffraction peak position while point defects results in local changes of the lattice parameter which together with crystallite size results in peak broadening. The out-of-plane lattice expansion, or contraction, is related to the film stress according to,

\[ \frac{d}{d_0} = (1 - \frac{\nu \sigma Y}{Y}) \], (15)

where \( d_0 \) is the stress free lattice parameter, \( \nu \) is the Poisson ratio of the material\(^*\), \( \sigma \) is the film stress and \( Y \) is the elastic modulus of the material.

It is possible to map the orientation of the crystallites in the film by measuring the scattered intensity from a certain lattice reflection as a function of the sample rotation (φ) and tilt (ψ) in a pole figure at a fixed scattering angle, 2θ. If the sample has a preferred orientation it is possible to use pole figures to find both the in-plane and out-of-plane alignment of its grains. Randomly oriented samples will, ideally, show the same scattered intensity regardless of sample tilt and rotation. Samples with an out-of-plane alignment but a random in-plane alignment.

\(^*\) When a material is squeezed (or stretched) in one direction it expands (contracts) in the directions perpendicular to the squeezing. The Poisson ratio is the relationship between how much it is squeezed and how much it expands.
orientation of the grains would show a sharp peak at zero tilt for the lattice plane parallel to the sample surface and rings at tilt angles corresponding to the angles between the lattice plane parallel to the surface and the measured planes. Samples with both in-plane and out-of-plane alignment of the grains would have intensity poles only at certain rotation angles, or angular ranges, depending on the degree of in-plane alignment.

4.1.1. The sin²ψ-method
Determination of film stresses from diffraction peak shifts is a method limited to equibiaxial in-plane stresses in defect free isotropic materials. If this is not the case peak shift analysis will be erroneous. A more robust method is the sin²ψ-method where the lattice parameter for a certain diffraction peak is measured for different sample tilts. When in-plane compressive (tensile) stresses are present in the sample the lattice parameter for planes parallel to the surface will be expanded (contracted) compared to the equilibrium lattice parameter while the lattice parameter for planes perpendicular to the surface will be contracted (expanded). The average strain in the crystallites relates to the tilt angle, ψ, and the stress, σ, according to

\[
\frac{d_\psi - d_0}{d_0} = \frac{1 + v}{1 - v} \sigma \sin^2 \psi - 2 \frac{v}{1 - v} \sigma, \quad (16)
\]

for a biaxially stresses film. Here \( d_\psi \) is the lattice parameter at tilt angle \( \psi \) and \( d_0 \) is the stress free lattice parameter. Plotting the measured lattice parameter, \( d_\psi \), versus \( \sin^2 \psi \) will according to equation (16) give a straight line where the slope of the line is related to the film stress and elastic properties, figure 15. By convention a negative slope signifies compressive stress while a positive slope signifies tensile stress. The elastic properties of materials are often anisotropic requiring modifications for equation (16) to take this anisotropy into account. This is done by introducing the so-called x-ray elastic constants, \( \frac{1}{2} S_1 \) and \( S_2 \), instead of the \( \frac{1 + v}{1 - v} \) and \( -2 \frac{v}{1 - v} \) terms respectively. The x-ray elastic constants are tensor quantities that take the directionality of the elastic properties into account. The strain free direction, \( \sin^2 \psi^* \), in the crystal can be determined from the x-ray elastic constants

\[
\sin^2 \psi^* = \frac{\sqrt{S_1 S_2}}{1 + S_2} \quad (17)
\]

the stress free lattice parameter, \( d_0 \), can then be determined from the \( \sin^2 \psi \)-plot. Film stress does not necessarily have to be acting in the plane of the film, growth induced point defects can give rise to hydrostatic stress resulting in an expansion of the lattice in all directions (c.f. section 2.4) and a triaxial stress state of the film. This is seen as a vertical shift of the \( \sin^2 \psi \)-
The value $d_0$ determined from $\sin^2\psi$ measurements is therefore not necessarily the actual stress free lattice parameter but rather the stress free but defected lattice parameter.

A $\sin^2\psi$ measurement requires measurement of the lattice parameter for a number of tilts, preferably in steps equally spaced steps of $\sin^2\psi$. This is usually not practically possible for films with a preferred orientation as the Bragg reflections from the lattice planes of interest only will be present at certain tilts. The crystallite group method has been developed to alleviate this limitation. Instead of measuring a certain Bragg reflection for a number of tilt angles a group of crystallites with a specific crystalline orientation is chosen. The lattice spacing is then measured for different lattice planes oriented at different angles $\psi$ and $\phi$ in the same grain, the lattice parameter then calculated for each $\psi$ resulting in a $d_0$ vs. $\sin^2\psi$-plot.

4.1.2. X-ray reflectivity

X-rays are reflected at interfaces of materials, for example the film-substrate interface or the film-air interface, when the incidence angle is sufficiently small and will interfere with x-rays reflected in the other interfaces if the path difference is even number of wavelengths. The results of two typical reflectivity measurement of a Mo film can be seen in figure 16. At small scattering angles, $< 1$ degree depending on the measured material, total external reflection occurs. The angle when the x-rays can penetrate into the material, the critical angle, is proportional to the electron density of the material, which in turn is proportional to the mass.
density of the material. At angles larger than the critical angle interference fringes, known as Kiessig fringes, are observed. Since they are the result of interference between x-rays reflected in the interfaces of the film the distance between the Kiessig fringes can be used to determine the film thickness. This distance is inversely proportional to the film thickness thereby limiting the maximum film thickness that can be measured to the resolution of the X-ray optics. The dampening of the measured reflectivity can be used to determine the surface and interface roughness of a film. The film thickness, roughness and density is usually determined by fitting the measured spectrum to a model taking many order reflections in the layer(s) into account. X-ray reflectivity have been used heavily in the work leading to this thesis both as a fast method to measure film thickness for deposition rate calibration but also to measure the surface roughness and the density of films.

4.2. Stress determination by substrate curvature measurements

A thin film in a stressed state has a driving force to expand or contract but is constrained by the substrate. As a consequence the film exerts force on the substrate causing it to bend. How much the substrate bends depends on the elastic compliance of the substrate, the substrate

![Image](image-url)
thickness and the film force per unit width that in turn depends on the average stress in the film and the film thickness as expressed by the modified Stoney equation [84,85],

\[ \frac{F}{w} = \sigma t_f = \frac{Y_s t_s^2}{6} \kappa. \quad (18) \]

Here \( F/w \) is the film force per unit width, \( \sigma \) the average film stress, \( t_f \) the film thickness, \( Y_s \) the biaxial elastic modulus of the substrate, \( t_s \) the substrate thickness and \( \kappa \) curvature of the substrate. Equation (18) shows that no information of the elastic properties of the film is needed to determine the film stress using substrate curvature measurements. The curvature method is therefore suitable for stress measurements of films with unknown elastic constants. It should also be noted that the substrate curvature method measures the stress in the full volume of the film, crystalline or amorphous, as opposed to the sin\(^2\)\(\psi\)-method, which only measures the stress in the crystalline parts of the film.

The curvature of the substrate can be measured in a variety of ways the most common being reflecting laser beams of the substrate and measuring their deflection. The particular setup used in the work leading to this thesis multi-beam optical stress sensor, figure 17, where a laser beam is split into a linear or square array of parallel beams using beam splitters. The laser beams are reflected off the substrate and their positions recorded using a CCD-camera.

The substrate curvature is calculated as

\[ \kappa = \frac{1}{R_s} = \frac{d-d_0}{d_0} \left( \frac{\cos \theta}{2L} \right) \quad (19) \]

for a line of spots parallel to the laser beams and

\[ \kappa = \frac{d-d_0}{d_0} \left( \frac{1}{2L \cos \theta} \right) \quad (20) \]
for a line of spots perpendicular to the laser beams. Where \( \kappa \) is the substrate curvature, \( R_c \) is the radius of curvature, \( d \) and \( d_0 \) is the spacing between the laser beams at the CCD and the initial beam spacing respectively, \( L \) is the distance between the substrate and the CCD and \( \alpha \) is the incidence angle of the laser beams.

The substrate curvature technique is easily adaptable for *in situ* measurements of the film stress evolution, the only requirements on the deposition chamber is that the measurements setup can be mounted on the chamber and that there is a free optical path between the laser, the substrate and the CCD. For in-situ measurements the curvature evolution is recorded as a function of time with the results usually presented in plots like figure 7 and 8 showing the stress-thickness product (\( \sigma t \)) or force-per-unit-width vs. film thickness, the stress-thickness product being calculated from the curvature at each point in time while the film thickness is determined from knowledge of the deposition rate. From such plots information of both the total stress in the film up to a certain thickness as well as the instantaneous film stress at any film thickness determined from dividing the stress-thickness product by the film thickness and taking the derivative of the curve at the point of interest respectively.

4.3. Atomic force microscopy

Atomic force microscopy is one of many scanning probe microscopy techniques and is used to characterize the surface topography of samples. The working principle is that a sharp tip is scanned across the surface in a raster pattern while the vertical position of the tip is monitored as the tip follows the surface profile to build up a height map of the surface as shown in figure 18. The tip is located at the end of a thin cantilever mounted on a piezoelectric scanner able to scan the tip laterally and vertically. Atomic force microscopy has three main modes of operation contact mode, tapping mode and non-contact mode. In contact mode the tip is put into contact with the surface and dragged across the surface while the deflection of the cantilever is monitored and kept constant. Contact mode AFM can result in damage of the tip and/or the surface resulting in erroneous measurements of the surface topography. Tapping mode AFM, also known as intermittent contact mode AFM, is gentler on the tip and sample than the contact mode. Here the cantilever is made to oscillate at or near its resonance frequency with constant amplitude. Height information is gained using the oscillation amplitude as a regulation parameter. The tip is lowered towards the surface until the oscillation amplitude decreases because the tip comes into contact with the surface, the height of the cantilever above the surface is then kept constant by the regulation as the tip is scanned.
across the surface. Non-contact AFM also utilizes an oscillating cantilever and amplitude regulation, here however the tip oscillates close to but not touching the surface. At these distances the tip interacts with the sample through attractive Van der Waals-forces causing amplitude shifts when cantilever height above the surface changes. In contact mode and tapping mode the tip penetrates the thin liquid layer present on surfaces exposed to atmosphere allowing for higher resolution imaging of surfaces than non-contact mode under ambient conditions. Tip effects need to be taken into account when interpreting AFM micrographs as they can result in image artifacts. Some examples are imaging sharp features using a tip with a radius larger than the feature radius, which results in an image of the tip rather than the feature, or that tips with more than one peak results in repetition of features.

Atomic force microscopy has been used for surface imaging and characterization of the surface morphology, in-plane grain size and surface roughness in Paper 2 included in this thesis.

4.4. Spectroscopic ellipsometry

Electromagnetic waves, such as light, incident on a surface interacts with free and bound electrons in the material producing a response that is governed by the complex dielectric functions $\varepsilon(\omega)$ of the material, where $\omega$ is the angular frequency of the electromagnetic wave. $\varepsilon(\omega)$ contains information not only of the optical properties of the material but also on electrical and physical properties [86]. Spectroscopic ellipsometry utilizes a wide band light source usually spanning a spectral region from near IR to UV light, although the exact
spectral range varies between setups. Light form a broadband light source is linearly polarized by a polarizer and passed through a compensator, figure 19, causing a phase shift between the components of the electromagnetic wave. It is then reflected in the sample where its polarization state is changes once again, now to an elliptical polarization where the polarization state is dependent on the interaction between the incident light and the substrate. After reflection the light passes through another compensator and fixed linear polarizer before falling into the detector. The measured quantity is called the complex ellipsometric ratio, $\rho$, and can be written as

$$\rho = \tan(\Psi)e^{i\Delta} \quad (21)$$

where $\tan(\Psi)$ is the amplitude ratio between the electric field components and $\Delta$ is the phase shift between the field components. The ellipsometric ratio can be used to calculate the effective complex dielectric function of the film-substrate system. The complex dielectric function cannot usually be used to directly calculate to optical constants of the film. Instead they are found using a mathematical model incorporating the known optical constants of the substrate and a dispersion relation modeling the optical response of the film. The calculated optical response of the model is then fitted to the measured data by varying the parameters of the dispersion relation. Different dispersion relations model light-matter interactions with varying degrees of physical accuracy. In empirical dispersion relations only some of the parameters have a physical significance such as e.g. refractive index and film thickness. Classical dispersion relations are derived form classical electromagnetic theory and can take free and bound electrons in the material into account to model some optical and electrical properties of the film. Properties such as band gap and defect states can be taken into account using quantum mechanical dispersion relations, which takes quantum effects into account in

Figure 20: Schematic of an ellipsometry setup.
addition to classical effects. The choice of dispersion relation should be done taking both the
degree of physical accuracy needed and convenience into account. In Paper 1 \textit{in-situ}
ellipsometry was performed to be able to find the thickness dependence of the electrical
properties of the Ag films. The film was modeled using a classical Drude term modeling the
free electrons in the sample to find the electrical resistivity at each film thickness.
5. SUMMARY OF APPENDED PAPERS

The results of the appended papers are summarized in this section. In Paper 1 it was shown that the HiPIMS discharge generates a pulsed deposition flux through time-resolved mass spectrometry measurements and Monte-Carlo simulations of particle transport. The influence of the pulsing frequency, instantaneous deposition rate and energetic bombardment on the nucleation and early growth of polycrystalline Ag thin films on SiO$_2$ was investigated using in situ stress measurements and in situ spectroscopic ellipsometry. It was shown that an increase of the instantaneous deposition rate resulted in a decrease in the thickness at which the film becomes continuous, which was explained by an increased nucleation density as a result of the increased instantaneous deposition rate combined with the increased energetic bombardment. Increasing the pulsing frequency also resulted in decreases of the thickness at which the film became continuous. Estimations of the adatom lifetimes and the island coalescence times showed that they coincide with the time between flux pulses for high pulsing frequencies. This results in an increase of the adatom and nucleation density and a retardation of island coalescence, all leading to a decrease in the film thickness where the film becomes continuous. It was also realized that measurements of the nucleation density in pulsed processes can be used to measure the adatom lifetimes, from which then can be used to find surface diffusion parameters.

Paper 2 investigated the effects of energetic bombardment on compressive stress generation in polycrystalline Mo films. It was observed that the magnitude of the compressive stress was connected to the flux and energy of the bombarding species. Stress measurements using the sin$^2$ψ-method showed that although the stress magnitude varied from -3.0 GPa to 0.2 GPa, the stress free lattice parameter was more or less constant for all deposition conditions and only slightly expanded, 0.1 %, from the bulk lattice parameter. It was therefore concluded that the compressive stresses were not generated by point defects induced by the energetic bombardment but rather by densification of the grain boundaries, which was confirmed film density measurements by x-ray reflectivity. A model explaining the densification process by bombardment induced surface and near surface diffusion of metal atoms into the grain boundaries was proposed.
6. CURRENT RESEARCH AND FUTURE PLANS

Both research projects leading to this thesis give rise to more questions and ideas for future investigations, some will be outlined here. Compressive stress generation through grain boundary densification is not a well explored area. The findings in Paper 2 can be extended on in several directions.

- The reversible stress relaxations observed under high mobility conditions have eluded explanation this far. Out diffusion of atoms from the grain boundaries have been suggested to be the explanation but this has not been possible to confirm. If this is true stress relaxations should also take place in dense films deposited under low mobility conditions when enough energy to activate grain boundary diffusion is provided.

- The magnitude of grain boundary densification induced compressive stresses should depend on the grain sizes. Deposition of films with different well controlled grain sizes should at the same bombardment conditions could therefore be used to confirm that grain boundary densification indeed is a source of compressive stresses.

- Tensile stresses generated by grain boundary attraction and compressive stresses generated by defects in the grains are additive. This should also be the case for compressive grain boundary stresses and compressive stresses generated by defects.

The results from Paper 1 can also be extended upon in a few different ways.

- The influences of energetic bombardment and instantaneous deposition rate were convoluted in Paper 1. It would be interesting to separate their influences on nucleation and early growth processes.

- Further manipulation of the nucleation processes could lead both to the formation of ultra-thin conductive Ag films or the formation of well separated Ag particles on the surface both having important roles in optical applications. Investigations into how far it is possible to go in both directions would also be interesting.
7. REFERENCES


