In-situ stress analytics at sub-nanoscale thin film growth

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Cover:

A view into the deposition setup while in operation. This is the deposition setup that is used for most of the results presented in this work. The plasma generated by the magnetrons lights up the inside of the deposition setup with a characteristic glow. The front page view looks from the bottom up towards the sample (not visible) via a mirror. The back page view looks from the side and is unique, as the top of the magnetron is visible. During normal operation this view is shielded to avoid deposition onto the viewport of the setup, only shortly after installation there was a moment when this shielding was not in place.

IN-SITU STRESS ANALYTICS AT SUB-NANOSCALE THIN FILM GROWTH

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Chapter 1

Introduction

"What I want to talk about is the problem of manipulating and controlling things on a small scale." This quote is from the introduction of the famous lecture of Richard Feynman titled "There's Plenty of Room at the Bottom", which he gave in 1959. In the lecture he addresses many aspects of the field of physics, biology and electronics at the atomic level and makes some remarkable predictions.

On the subject of miniturizing the computer he makes a very interesting remark: "For instance, the wires should be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across.". Nowadays computer chips, such as the Central Processing Unit (CPU), are produced with a 7 nm feature size, falling in the range Feynman predicted in a time where the DEC PDP-1 was just introduced, a computer build with 2700 transistors and 3000 diodes, with a 4096 word magnetic core memory and the size of a large cabinet.

In this work we will focus not on structures that are small in 2 dimensions (wires), but only those that are small in one dimension (layers). Feynman was already fascinated by this: "What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can't see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do." The large area of research on thin film physics proves his prediction is correct.

The research area of thin films spans film thicknesses ranging from a fraction of a nanometer to tens of micrometers. This makes the field of thin film physics a very wide and diverse field, ranging from cosmetic coatings on consumer products to single atom epitaxial layers for fundamental research. The process of applying a thin film onto a surface is called deposition. In this process many physical phenomenon occur on a nanometer to atomic length scale. These processes occur over the full surface of a thin film, resulting collectively in macroscopic effects. In this thesis we focus on the intrinsic (i.e. from the deposition process) stress, specifically the stress that

occurs during the interface formation and the initial layer growth of several nm. The stress is a macroscopic effect which applies a force on macroscopic objects (such as a cantilever) but which originates from microscopic effects with a length scale typically around the layer thickness, which can be as low as the interatomic distance (in case of chemical bonding, grain boundaries, interstitials) or much larger than the layer thickness (in case of polycrystalline growth with a large lateral grain size). It can therefore also be used to study processes at these length scales which are important in many application, of which a few are given later on in this chapter.

In this chapter a selection of the wide range of applications of thin films is given. The deposition methods are discussed as these affect many growth properties. The growth itself can be classified in different growth modes, of which a selection is discussed. The physics playing a role in these growth modes also serve as one of the origins of stress. Several applications where stress is relevant are discussed, as well as failure mechanisms which can occur in certain applications.

The scope of the thesis is then described to explain the contribution of this thesis to the field of thin film physics. This is followed by an outline of the thesis, after which the valorisation of the work presented is discussed.

1.1 Thin film applications

Thin films have a wide range of applications and are more a part of daily life than one might think. Thin films can range in thickness from a fraction of a nanometer to hundreds of micrometers (in case of wear-resistant or decorative coatings). In this work we focus on thin films in the nanometer regime, therefore in this section a small list of applications is gathered to illustrate the broad spectrum of applications of these thin films. Even if the materials in this work are not always the ideal materials for these applications, the analysis tools and methods used in this work can be applied broadly.

The properties of thin films can differ strongly from the bulk behavior, while being made of the same material. For example electrical, mechanical, thermal and optical properties can be different in thin layer or thin layer structures. In many cases they can be tuned to fit their application, but unfortunately in many cases the properties can also be undesirable.

Thin layers can be used to prevent chemical reactions, such as protective layers that prevent the underlying material from oxidising. Such protective layers typically must be very thin (down to several nanometer) to prevent them from interfering with the functional behavior of the underlying structure. Thin layers can also be used to promote chemical reactions in case of a catalyst. As only the surface of the layer is active its thickness can be very small, reducing the cost of the needed material[1]. In addition, rough or porous structures can be deposited, providing a large surface area in a small volume which improves efficiency[2].

The thermal emissivity of a material depends on its outer surface. For many large bulk devices a paint can be used to determine this property, far from a thin layer. For smaller and thinner devices, such as free standing membranes, the thin film must be thin (several nm) compared to the device thickness in order not to modify its properties. As the membranes themselves are already thin, the stress of any additional layer will have a major impact on the stress of the entire system.

Semiconductor integrated circuit devices consist of patterned layers of conducting, isolating or semiconducting layers, giving the device its function. With the continuing shrinking of the feature sizes the interfaces of the thin films involved become more and more important.

Optical coatings typically consist of layers with thicknesses comparable to the wavelength they are made for. For example, a single layer anti-reflection coating can be made with a $\lambda/4$ thickness layer with a refractive index of $n_{coating} = \sqrt{n_{substrate}}$. For reflective surfaces for visible light a single metallic layer can be used. Although a cheap and broadband solution, its performance (reflectivity, damage threshold) is limited. For higher reflectivity or wavelength selectivity a Bragg reflector can be used. A Bragg reflector consists of alternating layers of high and low index of refraction. The reflections at each interface interfere constructively, resulting in a reflectivity that can reach 99.999% or higher for a narrow wavelength range. Bragg reflectors are used over a large wavelength range far beyond the visible light, from infrared to XUV. For short wavelength imaging systems the layer thickness used in the Bragg reflector are often in the (sub)nanometer range. On this thickness scale the interface between the individual layers can have a large impact on the device characteristics, such as reflectivity and stress.

1.2 Deposition Methods

Applying a thin film onto a substrate can be done using various methods. For the deposition of thin films in the order of several nm to tens of nm typically vapor deposition techniques are used as these provide a high uniformity and a high control over the deposition rate, which typically ranges from from 0.1 to 10 nm/s, allowing thin films to be deposited accurately. These methods can be coarsely divided in two categories, Chemical vapor deposition and physical vapor deposition. A short description of several methods is given in this section to give an introduction into the methods that are available and to highlight properties of the method that were important in choosing the deposition method used in this work.[3].

1.2.1 Chemical vapor deposition

Chemical vapor deposition (CVD) uses chemicals reaction to grow a thin film onto a substrate[4, 5]. This is done by introducing a precursor into

the reaction chamber where the substrate is mounted. The precursor reacts and/or decomposes at the substrate surface. CVD is suitable to grow materials with a wide range of physical, tribological and chemical properties by varying experimental parameters such as the substrate material and temperature and the gas composition and pressure. The vapor deposition can be assisted by for example a plasma source to initiate or maintain the chemical reaction.

As CVD is a chemical process the growth is conformal, i.e. with proper conditions, such as gas flow and temperature, all surfaces of the substrate receive an equal deposition flux. This is useful to deposit on high aspect ratio or 3D structures. CVD can also be used in a distinct chemically selective mode to precisely control the number of monolayers deposited. In Atomic Layer deposition (ALD) self-terminating reactions are used to limit the layer growth to one monolayer at a time[6].

CVD typically requires temperatures of several hundred degrees. This may limit its applicability since many thin film applications, such as the Mo and Si based layered systems studied in this work, suffer from strong intermixing and thermally induced compound formation at such elevated temperatures. In addition CVD typically is not suitable to deposit high purity metallic thin films[7].

1.2.2 Physical vapor deposition

In a Physical Vapor Deposition (PVD) process solid materials are vaporized in a vacuum and deposited onto the substrate. A short description of several common PVD processes is given in this section[3, 8].

In thermal evaporation, such as Electron Beam (often referred to as E-beam) deposition, the target material is heated until it evaporates. This creates a stream of low energy (thermal) particles that deposit very directionally, i. e. in a line of sight from the deposition source. E-beam deposition is suitable to create low roughness thin films, as due to the low (thermal) ad-atom energy no island formation occurs. However, the layers formed have a lower density than for example magnetron sputter deposition due to shadowing of voids by already deposited atoms. By using Ion Beam Assisted Deposition (IBAD) or an Ion Beam Polishing (IBP) step after deposition the density can be increased, which also lowers the roughness [9].

Pulsed Laser Deposition (PLD) uses a high power laser that strikes a target of the material to be deposited[10]. This vaporizes part of the target material and creates a plasma plume. The substrate is located in the path of the plasma plume to let the target material condense and grow the thin film. PLD allows to keep the stoichiometry of the thin film that is growth equal to the target stoichiometry, which is useful when growing oxide films, but often oxygen presence is needed to keep the stoichiometry. PLD is typically used for crystalline growth on heated substrates to increase ad-atom mobility.

Magnetron Sputter Deposition (MSD) uses a plasma that is confined to the sputter target by magnets[11, 12]. The plasma, typically generated using an inert process gas (also referred to as sputter gas), consists of electrons, neutral atoms and differently charged ions. The sputter gas ions accelerate towards the target, resulting in the ejection (also referred to as sputtering) of target material. The sputtered atoms typically have energies of several to several tens of eV. The mean free path length of the sputtered atoms is determined by the sputter gas pressure and typically smaller than the target to substrate distance. The mean free path length determines the number of collisions of the sputtered atoms with the sputter gas and therefore the energy of the sputtered atoms upon arrival at the substrate. The process parameters of MSD can therefore be used to optimize the layer growth to obtain smooth and dense layers. MSD is a very stable process which allows layered structures, such as multilayer mirrors, to be deposited with high accuracy in periodicity and high purity. A substrate bias can also be used to attract ions from the plasma. MSD is compatible with many materials that are conductive or isolating by using DC or RF MSD.

The work presented in this thesis therefore uses magnetron sputter deposition, the deposition setup used is further detailed in chapter 2.

1.3 Growth modes

The growth mode of a layer describes the movement of the atoms of the layer being deposited and the resulting structure. The movement depends on the energies and attraction forces of the ad-atoms and the substrate. In this section a short overview of a few common growth modes is given[13].

In case of a thermodynamic equilibrium the film growth is determined by the attraction between the ad-atoms themselves and the attraction between the ad-atoms and the substrate. This results in the three well-known growth modes[14, 15], as listed below. The growth in case of these thermodynamic growth modes is epitaxial, meaning that the substrate is crystalline and the ad-atoms form a layer that conforms to the lattice spacing. This means the lattice of the added layer is coherent with respect to the lattice of the substrate.

In the Frank-van der Merwe (FM) growth mode the atoms grow layer by layer. For FM growth to occur the ad-atoms must be more attracted to the substrate than to other ad-atoms, driving them to fill incomplete layers before nucleating a new layer. The mobility of the ad-atoms must be sufficiently high to allow this to occur.

For the Volmer-Weber (VW) growth mode the interaction between ad-atoms is stronger than the interaction of the ad-atoms with the substrate. The ad-atoms therefore tend to cluster and form 3D islands. As these islands increase in size they coalesce, forming a closed layer.

The Stranski-Krastanov (SK) growth is an intermediate growth mode. The initial growth is layer-by-layer until a certain critical thickness where the growth transitions to island based growth. The critical thickness depends highly on the chemical and physical properties of the substrate and ad-atoms materials, such as the surface energy and the lattice parameters.

In most cases however, the growth condition are far away from thermodynamic equilibrium and dominated by kinetic effects, such as defects, impurities, nucleation around defects and randomly oriented facets of crystallites. These growth conditions are typically used due to the demands for a lower process temperature[16], which is applicable for the Mo/Si structures used in this work. The growth in this regime is commonly described by Structure Zone Models (SZM)[16, 17, 18, 19], for example by Thornton et. al.[20], which mainly take the mobility of ad-atoms into account, which is affected by the substrate temperature and melting temperature of the ad-atoms, as well as several other specific process conditions.

Besides the homologous temperature (the ratio between the substrate and melting temperature), the deposition rate, impinging particles and the background pressure also play a role. For low mobility ad-atoms (zone Ia), the growth is driven by a hit-and-stick mechanism. Self-shadowing can create void which are not filled due to the low ad-atom mobility, leading to porous films and a low density. Providing kinetic energy (by for example an ion flux) can suppress the void formation (zone Ib). Once the mobility is high enough the impinging atoms can nucleate and form a poly-crystalline layer (zone Ic). At higher temperatures the mobility becomes larger enough to support diffusion between grains (zone T) or even restructuring (zone II)[21].

The SZM describe poly-crystalline growth of relatively thick (hundreds of nm) layers and are not aimed at the initial growth occurring in the first several nm[22], which is investigated in this work. The MSD process used produces ad-atoms with several eV to a few tens of eV energy, sufficient to density the deposited layer. The mobility however is still low, resulting in a so-called stochastic growth mode, driven by the hit-and-stick mechanism, which prevents island formation which would lead to an increased roughness. A typical result for the systems presented in this work is a 0.2 nm RMS roughness (determined by AFM measurement) for layer systems of a few tens of nm, demonstrating the low roughness obtainable in this growth mode and excluding significant island formation.

1.4 Thin film stress

1.4.1 Origins of stress

Thin film stress can have various origins, ranging from intrinsic stresses introduced during device manufacturing, to stresses originating from specific device usage, such as thermal stress or mechanically applied stress.

The intrinsic stress is the stress that is present in the thin film due to the deposition process. The deposition method has a large influence on the growth mode and therefore the intrinsic stress. A porous growth is generally tensile while a dense layer is more compressive. The ad-atom energy or ion bombardment (either by an ion gun or backreflected neutrals from a magnetron) may result in a peening effect that densifies the layer and introduces compressive stress..

Chemical interactions also affect the stress, such as interface formation or passivation. Unintended chemical interactions can be oxidation in atmosphere after the deposition has finished and the sample is taken out.

Implantation of atoms introduces a compressive stress as the already deposited layer is densified. Diffusion or segregation also adds a doping to a layer but its mechanics are not straightforward as these processes can affect the growth of the layer being deposited.

The microstructure of a thin film has a significant impact on the stress. The different stages of the VW growth mode (island growth, coalescence and growth of the closed layer) result in a compressive, tensile and compressive stress, respectively, which is characteristic for VW growth.

In case of hetero-epitaxy the substrate and deposited atoms species differ. In case of a FM growth mode this results in a coherency stress, which is the result of the ad-atoms having to conform to the lattice spacing of the substrate, resulting in a compressive stress if the lattice spacing of the ad-atoms is larger (in a relaxed state), and tensile if the lattice spacing is smaller.

Materials such as W, Ta and Mo show an amorphous to poly-crystalline phase transition at room temperature, of which W and Mo show a tensile stress step[22]. The stress in poly-crystalline growth originates from both the grains as well as the grain boundaries, and grains can show different evolutions during growth depending on the material properties and sputter gas pressure[20].

1.4.2 Applications of thin film stress

The stress can be used to tune layer properties, such as the conductivity[23, 24], optical response[25] and magnetic properties[26, 27].

Tribological coatings are used to reduce wear of mechanical parts. The coatings must have a strong adhesion in order not to fail under friction forces. Even though the relationship between the intrinsic stress of the coating and the applied mechanical stress is not yet well known[28], stress engineering is necessary to obtain the correct tribological properties. Stress engineering can be performed by for example varying the deposition conditions, such as substrate temperature or process gas pressure, to affect the microstructure which results in a different intrinsic stress.

In optical applications of thin films, the stress must be accurately predictable in order to have negligible or a controlled surface deformation.

Especially in large short-wavelength optics, such as soft X-ray space telescopes, the exact surface shape is critical and the coating is a multilayer with many layers and interfaces, each with its own stress development during growth, and all contributing to the macroscopic mechanical forces acting upon the substrate.

Unfortunately stress can also induce failure in thin films. Although for many materials the stresses in thin films can exceed the tensile strength of the same material in bulk form without failing[20, 29], failure due to too high stresses can still occur. High tensile stresses can cause the thin film to crack, high compressive stresses can cause buckling, blistering or delamination of the thin film, sometimes already during device manufacturing.

In various device applications, and sometimes already during device manufacturing, the stresses in thin films can exceed the tensile strength of the material and cause the thin film to crack.

In particular for applications that require free standing films (e.g. x-ray windows for synchrotron beamlines), the stress is critical for mechanical stability. A compressive stress will cause wrinkling, which in many cases is detrimental to the performance of the device. A small tensile stress will pull the membrane flat, but a too high tensile stress will break the membrane. Stress engineering is therefore often necessary.

1.5 Scope and outline of the thesis

In this work we focus on the intrinsic stress of thin films ranging from 0.1 nm to 10 nm for Mo/Si based systems, the role of the substrate in the stress development and the interface formation occurring in these systems. The layers are deposited by magnetron sputtering and grow with a stochastic growth mode.

In chapter 2 the fabrication method used is introduced in more detail as well as the metrology methods that are used. The *in situ* stress measurement tool used for the measurements in chapter 4 and 5 and its development is described in this chapter as well.

In situ stress measurements are typically done by measuring the curvature of a substrate[14, 30, 31, 32]. The development of a self-contained *in vacuum in situ* thin film stress measurement tool is described in chapter 3. This tool enabled *in situ* stress measurement on a deposition setup without any modification to the deposition setup, where typically an electronic infrastructure is needed or an optical line of sight[33, 34, 35, 36].

The measuring the stress development of Mo/Si systems was pioneered by Freitag et. al. [37], revealing that the Mo layer grows mainly tensile while the Si layer growth compressive, partly cancelling eachothers stress. Large initial tensile and compressive stresses were found in the Mo and Si layer respectively, suggesting interface formation. The interface formation of the Mo/Si system is known and investigated[38, 39, 40, 41, 42, 43], for

example by ARXPS[44], but was not investigated in detail from a stress perspective. In chapter 4 the *in situ* stress measurements are combined with Low Energy Ion Scattering (LEIS) measurements to study the interfaces in Mo/Si systems. The combination of measurement methods is used to analyze growth stresses and interface formation and improve the understanding of the deposition related processes that occur during formation of these particular interfaces.

The growth of Mo on Si is affected significantly by the interface properties which is widely investigated in literature. However, the detailed mechanisms of the interface formation and the role of the substrate (or previously deposited layer) on the growth of the new layer are not well known. In chapter 5 the stress development of Mo is studied by modifying the interface properties by inserting an interlayer of either C or Ru. By performing the analysis for a range of interlayer thicknesses the gradual modification of interface properties is investigated. The study clarifies the role of the a-Si surface on which the Mo is deposited regarding diffusion and interface formation on the stress development of Mo.

The *in situ* XRD study of Mo is used to investigate the kinetics of the Mo phase transition, resulting in a model for the crystallite growth[45]. Chapter 6 expands on this work and focuses on the effect of the sputter gas pressure used during the Mo deposition in order to study the dependence of the amorphous to poly-crystalline phase transition on the pressure. This chapter describes the experimental aspects as well as the results of the experiment. The crystallization transition is also analysed by fitting the Mo (110) peak using a two component fit. In this fit a linear combination of two curves is fitted to the signal in order to separate the amorphous and poly-crystalline contribution during the transition.

1.6 Valorization

The instrumental work which was at the basis of this thin film research, has brought the known principle of laser beam deflection from deposited, and hence curving cantilevers, to a practical, high-resolution stress measurement tool. As such it has enabled high sensitivity stress measurements in systems that otherwise could not be assessed. The development of a self-contained in-vacuum *in situ* thin film stress measurement tool enables stress measurements on deposition setups without modification to the deposition setup. Typically a viewport either at normal incidence needs to be installed for deposition setups with a stationary or rotating sample. For deposition setups with a moving substrate significant infrastructure is needed to bring any optical or electrical signal to the substrate. By making the metrology tool self-contained and vacuum compatible no feedthroughs are needed. The metrology tool developed and described in this thesis therefore enables stress engineering where this is otherwise very difficult due to the

lack of *in situ* measurement options.

The tool has the potential to act as a general metrology platform. Measurement options such as a Faraday cup, a Langmuir probe or a quartz mass balance could be integrated. Also sample heating and bias can be implemented if the deposition setup itself has not support for this. For deposition setups with moving and rotating substrates this is generally challenging to implement.

The understanding of Mo/Si system interface formation and stress development is improved by the new method of correlating *in situ* stress development measurements with LEIS measurements. The role of the interface is also investigated by inserting C or Ru interlayers. Together this can improve the understanding of thin film growth and allow more effective stress engineering for applications using Mo/Si systems, such as MEMS or short wavelength optics. The methods presented can also be used to gain understanding on other thin film systems, widening the applications of the methods presented.

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Chapter 2

Experimental

This chapter describes the main experimental set-ups used for the measurements and the results later reported in chapters 4 and 5, including the deposition method, in-situ stress measurement setup development and metrology.

2.1 Magnetron sputter deposition setup

Stress measurements of thin films are not coupled to a certain deposition technique, although differences in the film properties are known to also depend on the deposition scheme. For all experiment performed in this work, Magnetron Sputter Deposition (MSD) was used, a physical vapor deposition process[1]. This is a deposition technique that is well known in industry for its stable and reproducible process, allowing layered systems to be deposited with highly accurate thickness. MSD requires an Ultra-High Vacuum (UHV) to reduce the contaminations on the substrate surface during deposition.

The MSD setup used for the results described in chapter 4 and 5 is described in more detail in this section. The setup used has a base pressure of $1\text{e-}8$ mbar, low enough that no influence of contaminations is observed. It features four movable 100 mm magnetrons to allow normal incidence deposition of four different materials without moving the substrate. DC magnetron sputtering is used as all materials used are conductive. Substrate rotation is possible for typical samples, for the in-situ stress measurements however the sample is kept stationary. The target to substrate distance is approximately 30 cm. The typical sputter gas pressure used is $8\text{e-}4$ mbar, resulting in a mean free path length comparable the target to substrate distance. The sputtered atoms can therefore reach the substrate without intermediate collisions that reduce the ad-atom energy. Due to the energy of the ad-atoms of several eV to tens of eV and the reflected neutrals of the sputter gas plasma the layers grown are typically smooth and dense.

All depositions are done at room temperature. As the magnetrons have a power of typically 500W a free hanging cantilever heats up by approximately 10 degrees above room temperature, measured by a thermocouple on the cantilever in a dedicated experiment. Even with the temperature at the surface being higher due to the deposition flux[2], this is expected to be low enough not to affect the ad-atom mobility on the substrate and below the temperature of thermally induced interface formation. A shutter controls the deposition time, which in combination with a calibrated deposition speed results in accurately deposited layer thicknesses. No bias voltage is applied to the substrate and the substrate is grounded to prevent charging effects.

The sputter deposition setup also allows co-deposition, ion bombardment during or after deposition, and thermal (E-beam) evaporation. Although the effects of these complementary deposition/surface modification

techniques on layer growth were investigated during the PhD work, the results are not included in this thesis.

2.2 Low Energy Ion Scattering

The details of the instrument used and the processing of the LEIS measurement results done can be found in chapter 4. A short summary of the LEIS measurement principle is given here to give a complete view in this chapter of the metrology used in this work.

The in-situ stress measurements must be linked to physical processes taking place in the thin films we investigated. To aid in the interpretation of the in-situ stress measurement Low Energy Ion Scattering (LEIS) measurements were done. Using LEIS the atomic composition of the sample surface can be determined [3]. This is useful to determine intermixing, compound formation and the closing of the deposited layer[4].

In-situ stress measurements provide a near continuous curve of the stress development. To link LEIS measurements to the in-situ stress measurements a deposition depth profile is created. The measurements were performed using a separate deposition setup with similar deposition conditions. The layer deposition was done at several thicknesses of the layer to be analyzed. For each thickness a separate sample was prepared to reduce contaminations.

The surface sensitivity of LEIS originates from the high probability of ions to be neutralized once they pass the uppermost monolayer[3, 5, 6, 7]. The scattering of the uppermost layer is elastic, the scattered ions therefore have a narrow energy spread depending on the atom they scattered off which is measured to determine the atom species. These peaks in the energy spectrum are used to determine the surface atomic fraction. Projectiles that penetrate the surface have a neutralization probability near 1 and lose energy proportional to the travel length inside the layer. If they scatter off a deeper lying layer and reionise this results in a low energy tail in the main peak and can therefore be separated.

2.3 In-situ stress measurements

This section describes the development of the in-situ stress measurement setup used for the structures described in chapter 4 and 5. The metrology tool described in chapter 3 is the successor of this setup but was not used to obtain the measurements presented in this work.

2.3.1 Requirements

The goal was to surpass the accuracy obtained by Freitag et. al. [8], where the noise in the experimental data is not low enough to properly identify

features such as the amorphous to poly-crystalline phase transition in the stress development, which is around 0.7 N/m as shown in chapter 3. A typical application would be to measure the stress of a Mo/Si multilayer, commonly used as Bragg reflector for short wavelengths. A full 50 period Mo/Si multilayer with a 6.7 nm period may have a stress up to 600 MPa, which must be within the measurement range without stopping the deposition process. The measurement range and noise requirement is therefore defined as >200 N/m range while resolving 0.5 N/m features. This includes uncertainties due to vibrations and thermal effects.

2.3.2 Method

There are several methods to determine the growth stress of a thin film during deposition. Indirect methods, such as Raman spectroscopy[9, 10, 11], are only applicable to a limited number of materials and require an accurate model of the layered system, which is often complicated due to complex interfaces. XRD or other diffraction based methods can only measure the stress inside polycrystalline layers[12], which limits their applicability. Measuring the bending of a cantilever under influence of the thin film stress is a direct method of determining the stress. The cantilever curvature and the thin film stress are related via Stoney's equation:

$$\sigma h = \frac{E_s h_s^2}{6(1 - \nu)} (\kappa - \kappa_0). \quad (2.1)$$

The cantilevers used in this work are cut from <100> Si wafers. The curvature induced the the stress σ depends on the material constants of the cantilever, specifically the Young's modulus E_s and the Poisson ratio ν , which are taken from [13]. The layer thickness h must be very small compared to the thickness of the cantilever h_s [14]. The initial curvature κ_0 is subtracted from the end curvature κ after deposition of the thin film to subtract the contribution of the cantilever itself to the final curvature. The cantilever curvature must not be influenced by its mounting. As thermal stress induces a curvature, this cannot be distinguished from the curvature due to the intrinsic stress, however, the effect of thermal stress was only significant for layer systems of several hundred nm thick. The thermal stress originated from the heat input of the MSD process and could be easily compensated by a simple thermal model.

The force per unit width (F/w) is defined as σh and is directly proportional to the measured curvature. The derivative of the force per unit width is the incremental growth stress expressed in N/m^2 and shows the stress of the newly added material but also includes any stress changes induced in the substrate layer by the added material. A linear stress development in a F/w curve during layer growth therefore indicates a material growth at constant stress. However, since numerical derivation introduces high noise levels F/w is used in this work.

Figure 2.1: Schematic overview of the optical setup, left: outside the vacuum, right: inside the vacuum system. The laser beam exits a collimator (1), is split by a beamsplitter (2) and with the use of a folding mirror (3) the two beams are sent into the vacuum system. The clamp (5) holds the Si wafer (6) of which the beams deflect. Two mirrors reflect the beam back along the same path (7), after which they are combined onto the camera (4).

The cantilever curvature can be determined with several methods. Electrical methods, such as a strain gauge or capacitive measurements, may receive interference from the magnetron sputter deposition process, which uses a pulsed DC high voltage[15]. Thermocouple measurements performed on a cantilever already suffered from significant interference, therefore electrical methods are expected to suffer from electrical interference as well. Accurate measurement would only be possible when the deposition is stopped, defying the purpose of the measurement. The starting and stopping of the deposition may also introduce errors (for example due to vibrations of the shutter opening and closing) that cannot be measured without an in-situ measurement.

Optical measurements are not affected by the deposition process and are commonly used[16, 17, 18]. Several methods are possible, for example interferometry[19, 20], using a wavefront camera[21], or a laser deflectometer[22, 23, 24]. A laser deflectometer was chosen due to the simplicity and robustness. The sensitivity of the laser deflectometer was also expected to be sufficient, as shown in the next section. An interferometer would achieve a much higher resolution but requires resolving fringes, which may result in unrecoverable error due to rapid movement due to vibrations during deposition.

A schematic overview of the optical setup used is given in figure 2.1. The cantilever was clamped at one side and free on the other to allow unimpeded curving of the cantilever. The clamping may however influence the cantilever, for example by varying clamping forces due to thermal expansion in the clamp or by shadowing the deposition flux close to the clamp. Therefore a dual beam laser deflectometer was used to be able to do differential measurements. By taking the difference in the deflection of two

laser beams, one near the clamp (approximately 10 mm away from it) and one on the end of the cantilever, any tilt of the cantilever is cancelled. As the measurement is only sensitive to the curvature between the two laser beams the flux shadowing of the clamp, which affects only a few mm near the clamp, is not influencing the measurement.

A fiber coupled diode laser of 635nm of 1 mW was chosen for its high beam quality (resulting in a small spot) and its practicality. A beamsplitter was used to split the laser beam into two beams before sending them into the vessel through a viewport. After deflecting off the cantilever, two mirrors inside the vessel close to the cantilever reflect the beams back via the same path they entered, deflecting a second time off the cantilever which doubles the sensitivity. The beams exit through the same viewport, minimizing the change needed to implement the stress measurement setup. Typical optical stress measurement devices require either a normal incidence or two viewports[18, 25]. The beams combine via the beamsplitter towards the camera (the beams towards the laser are unused), allowing a single camera to capture both beams. Overlap on the camera is prevented by giving one of the beams an out-of-plane offset.

2.3.3 Sensitivity and noise

The sensitivity of the optical stress measurement setup is defined as the beam movement on the camera for a given cantilever curvature. A larger sensitivity therefore also means a smaller total measurement range (in N/m), which is determined by the travel length of the beams on the camera before they clip on the edges of the sensor, after which their position cannot be determined accurately. The noise level is measured by taking the RMS value of the measured stress just before the start of the actual deposition and is used as performance metric. The period before the deposition start was preferred above the period of no deposition inbetween the layer depositions to allow analysis drift on longer timescales. In both cases the system is in a representative state for the actual deposition. The noise likely scales inversely with the sensitivity as the noise likely originates from the accuracy in determining the beam position and not from uncertainties in the actual cantilever curvature.

The sensitivity is proportional to the path length after deflecting off the cantilever, the number of deflections and the separation between the beams. A path length of 1 meter after deflection, 2 deflections (with minimal path length between them) and a 50 mm beam separation is used to obtain a high sensitivity. The estimated sensitivity was 1 pixel on the camera, corresponding to a 5 μ rad accuracy or a 0.2 N/m stress change for the configuration used in case of a 525 μ m wafer. According to Stoney's equation the sensitivity scales with the cantilever thickness squared. The material of the cantilever also influences the sensitivity via the Youngs modulus and Poisson ratio, however only silicon was considered as it is the industry standard

and due to the easy availability of low roughness substrates (typically 0.15 nm RMS).

The range obtained is approximately 350 N/m and 35 N/m for 525 μm and 150 μm thick cantilevers, respectively, corresponding to a 24 m radius of curvature of the cantilever. Using a 525 μm cantilever is therefore needed when a full Mo/Si multilayer stack needs to be measured. For investigating the stress development of single layer with a high resolution the 150 μm cantilever is suitable. The RMS noise obtained is 0.15 N/m when using 525 μm thick cantilevers and 0.012 N/m when using 150 μm thick cantilevers, which is sufficient to resolve 0.5 N/m features, meeting the requirements. The low noise of the 150 μm cantilever allows more fine details of the stress development to be captured by the measurement. The signal to noise ratio for even the smallest features observed was such that further improvement was not deemed useful.

2.3.4 Integration

The stress measurement was integrated into the existing deposition setup. The optics were placed on a breadboard attached to the flange of the vacuum viewport. The breadboard can be detached to allow a bakeout of the deposition setup without the optics attached as the components cannot withstand a 150 degree bakeout. The cantilever clamp and back reflecting mirrors are placed on a single assembly that replaces the regular sample holder. Sample rotation was disabled as the alignment must remain fixed. Shielding tubes were installed to prevent deposition on the viewport and the two backreflecting mirrors. The cantilever reflectivity depends on the material coated. The variation was typically 20%, small enough not to require compensation.

2.4 Other metrology

2.4.1 Optical surface profiler

The sensitivity of the in-situ stress measurement setups depends on the alignment uncertainty of the setup, in particular the separation between the two beams on the cantilever. As a realignment is needed due to small differences in the clamping conditions, small changes in the sensitivity may occur. When a different wafer thicknesses is used this requires a realignment as well, due to the different sagging of the cantilever due to gravity. To avoid measurement inaccuracies an optical surface profiler is used to obtain an absolute calibration of the stress measurement of each deposition run. This is done by measuring the curvature of the cantilever used for the in-situ measurement before and after the deposition. The change in curvature is induced by the thin film deposited and is calculated to a stress value. The in-situ measurement is then scaled such that the difference between

the start and end of the in-situ measurement is equal to the total stress measured by the optical surface profiler.

Measurements during venting of the deposition setup are not possible due to the large beam movement that occurs when the vacuum vessel of the seposition setup warps due to the change in pressure. Effects of exposure to atmosphere are therefore not corrected for. Therefore the depositions are always terminated with a suitable material to cap the thin films to minimize oxidation. The oxidation on the surface then only introduces a minimal stress change compared to the total stress of the deposited film. This could be investigated by introducing oxygen at low pressures into the system and measuring the stress change.

The optical surface profiler used is a Zygo Newview 7000 series White Light Interferometer (WLI). It provides a height map of the sample provided the sample is reflective at the wavelength range used. The instrument has a lateral resolution similar to an optical microscope and a sub nm depth resolution. This instrument has a field of view of approximately 12 mm when using the 1x magnification and the 1x zoom tube. By stitching together measurements a full cantilever can be measured.

The measurement principle of the WLI instrument is a broadband Michelson interferometer. A broadband light source illuminates the sample through the microscope objective. Inside the microscope objective is a beamsplitter and reference mirror. The incident light is split and sent to both the sample and reference mirror. Upon reflection both are combined and imaged onto a camera. As the light source has a very short coherence length constructive interference only occurs when the path length are equal. Due to the short coherence length only very little fringes are visible and the ambiguity of the fringe pattern from a monochromatic source is removed. The interference only occurs for equal path length, therefore the objective to sample distance is scanned while recording the interference pattern. From the recording a 3D surface profile is reconstructed. The cantilever curvature is calculated from this surface profile.

2.4.2 AFM

The surface morphology and roughness depends on the growth mode. In case of the stochastic growth mode no island formation and a very low roughness is expected. The detailed surface morphology is not directly studied in this thesis. The surface roughness was measured to verify the low roughness, which is important to verify the stochastic growth mode. A higher roughness also affects the energetic balance of the Mo phase transition, which depends on the stabilization of the amorphous phase by the interfaces. The typical roughness measured was 0.2 nm RMS, agreeing with a stochastic growth mode

The AFM measures the surface profile by scanning a nanometer sharp tip across the sample surface[26]. The spatial resolution is determined by

the sharpness of the tip. The tip is scanned in a line by line fashion across the scanning area while recording the tip height. The tip is attached to a cantilever so that the deflection of the cantilever by the tip going across the sample surface is measurable. The AFM is typically operated in tapping mode, which uses an oscillating cantilever that is only momentarily in contact with the sample surface. This prevents fast wearing of the sharp tip.

2.4.3 XRR and XRD

The length scales in the physical processes significant for thin film growth vary from the interatomic distance (typically in the order of 1 angstrom) to the layer thickness (typically 5 nm in this work). To probe the structure at these length scales X-rays are used. The Cu-K α line used has a wavelength of 0.154 nm, which is suitable for the structures used. Two methods are used, X-Ray Reflectivity (XRR) and X-Ray Diffraction (XRD).

XRR is used to calibrate the deposition rate by measuring the reflectivity of a multilayer stack under grazing incidence. The Bragg reflection angle corresponds to the multilayer periodicity. By depositing several multilayers with one component increasing in thickness the multilayer period increases proportional to the increase of the component. The increase in period corresponds to an increase in deposition time, from which the deposition rate can be determined. The advantage of this method is a much stronger and well-defined XRR signal which increases the accuracy and has no influences of interfaces or roughness typically present in thick layers.

XRD is used to measure the crystallinity of the Mo layers. To verify the thickness at which the amorphous to poly-crystalline phase transition occurs several samples with increasing Mo thickness were deposited. A Mo/Si multilayer was used to increase the signal strength. The samples were measured using a lab diffractometer. In case of amorphous Mo only two broad peaks are visible near the (110) and (211) peak position, due to the nearest neighbour distance. For poly-crystalline Mo the (110), (200), (211), (220), (310) and (222) are all visible, indicating the typical long range coherence.

The in-situ XRD measurements of chapter 6 were performed at the MPI beamline at the ANKA synchrotron at the Karlsruhe Institute of Technology (KIT). The experimental aspects of these measurements are presented in the same chapter.

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Chapter 3

Self-contained in-vacuum *in situ* thin film stress measurement tool

Abstract

A fully selfcontained in-vacuum device for measuring thin film stress *in situ* is presented. The stress was measured by measuring the curvature of a cantilever on which the thin film was deposited. For this, a dual beam laser deflectometer was used. All optics and electronics needed to perform the measurement are placed inside a vacuum-compatible vessel with the form factor of the substrate holders of the deposition system used. The standalone nature of the setup allows the vessel to be moved inside a deposition system independently of optical or electronic feedthroughs while measuring continuously. A Mo/Si multilayer structure was analysed to evaluate the performance of the setup. A radius of curvature resolution of 270 km was achieved. This allows small details of the stress development to be resolved, such as the interlayer formation between the layers and the amorphous-to-crystalline transition of the molybdenum which occurs at around 2 nm. The setup communicates with an external computer via a Wi-Fi connection. This wireless connection allows remote control over the acquisition and the live feedback of the measured stress. In principle, the vessel can act as a general metrology platform and add measurement capabilities to deposition setups with no modification to the deposition system.

3.1 Introduction

The physics of thin film deposition is an active research area with many properties remaining to be characterized. One important property is the intrinsic stress. Various macroscopic properties, such as electrical conductivity[1], optical response[2] and mechanical quality[3], all depend on the stresses that develop during thin film manufacturing. Among the mechanical failure mechanisms, strong compressive stress can lead to delamination whereas strong tensile stress can lead to cracking. Therefore, stress engineering is important for many applications such as hard coatings on machining tools[4], solar cells[5], micro electronics[6] and multilayered coatings for XUV optics[7].

In situ measurement methods can offer a wealth of information on the development of the layer during deposition. Thin film stress is directly related to the layer structure and composition, and measuring the development of stress during growth can provide information about layer growth properties such as island growth[8], compound formation[9] and crystallization[10]. In general, optical measurement techniques are favored over electrical methods such as capacitive deflection measurements because laser beams experience no interference from the plasma used in many deposition processes[11]. This makes the setup usable in all PVD processes. CVD processes are not directional and also coat the backside of the cantilever, resulting in no curvature change as well as coating the optical windows of the measurement beams.

Most of the optical *in situ* stress measurement setups are based on the use of a light path that starts and ends outside the deposition chamber and as such require a line of sight to the substrate[12, 13, 14, 15], which is generally stationary during the measurements. However, many coaters rotate the substrate to increase the uniformity of the deposited layer. Optical measurement techniques can be triggered by the rotation of the substrate[16, 17, 18] to enable measurements, but this limits the measurement rate to the rotation frequency and requires short integration times where long integration times are preferable for averaging out vibrations. A further complication arises when the substrate moves through the chamber in a planetary motion. To our knowledge there is currently no *in situ* stress metrology tool available that can function in such an environment.

In this work, we present an optical *in situ* stress measurement setup capable of working in a vacuum deposition chamber where the substrate can make any type of motion. This was done by integrating all measurement optics and electronics in a vacuum compatible vessel that remains at atmospheric pressure. Due to its stand-alone nature, the setup requires no electrical connection or optical feedthroughs and can operate fully isolated. This eliminates the need for extensive infrastructure to enable the measurements, and the setup can be integrated into existing deposition systems without their modification. The curvature of the cantilever sample

Figure 3.1: The vessel placed on a stand, showing two of four 4 KF16 flanges on the sides. The two holes on the sides and the pin on top are for handling the vessel by a loading mechanism in the deposition system

was determined by measuring the deflection of two lasers beams off the cantilever, which by using Stoney's equation was converted to a stress value. We discuss the vacuum and mechanical aspects, the design of the laser deflectometer, the electronics, the influences of the environment inside a deposition system and the Wi-Fi communication implemented. This is followed by several demonstration stress measurements performed using the setup. The stand-alone nature of the measurement setup makes it an ideal platform to integrate many more measurement capabilities into that might otherwise not be available in a deposition system, such as a Faraday cup, a Langmuir probe or a quartz mass balance.

3.2 Design of the *in situ* stress measurement setup

The design of the *in situ* stress measurement setup covers several aspects: vacuum technology, optical measurements, communication and the environmental conditions.

3.2.1 Vacuum and mechanical

The setup was designed in the form factor of a substrate holder of a Roth & Rau MS1600 deposition system (see figure 3.1). Achieving compatibility with the deposition system also imposed a weight limit of 20 kg. During the thin film deposition process, the substrate was sequentially moved over the stationary magnetrons for deposition of each layer while the substrate was rotating along its own axis to ensure homogeneous deposition over a large substrate area. The internal space available is approximately 25 cm in diameter and 15 cm high, and houses the electronics and optics.

The vacuum vessel shields the vacuum of the process chamber from those components that are not vacuum compatible and provides a suitable atmosphere for electronic components that can only function at atmospheric pressure. The vessel itself was made of aluminum and sealed with viton o-rings. Filling the vessel with helium and introducing it into the process chamber showed no increase in He in the RGA spectrum, indicating a negligible leak rate.

The vessel has several feedthroughs. At the bottom are two windows situated behind the cantilever to pass the optical beams out and into the vessel. At the side four feedthroughs are available. One was used for the Wi-Fi antenna. The option to add a second antenna at the other side of the vessel existed but the connection was already stable with only one. The other feedthroughs can be used for other purposes; for example, passing a thermocouple for external temperature measurements or to allow charging of the batteries without opening the vessel.

3.2.2 Optical

Setup/component choice

The curvature of the cantilever sample is proportional to the intrinsic stress of the deposited layer. Detection of the cantilever curvature was achieved by deflecting two laser beams off the cantilever and measuring their position using a camera after a certain propagation length. The difference in deflection is proportional to the curvature of the sample inbetween the beams. The beam near the clamp has little deflection and is therefore used as reference for the beam at the end of the cantilever. The optical system is shown in figure 3.2. Using only two beams allows for a simple optical design and allows for the tilt of the whole cantilever, for example by thermal expansion effects in the clamp, to be cancelled out by measuring the position of the beams relative to each other[19]. The cantilevers used are cut from <100> Si wafers and are 25 x 90 mm in size. Clamping the cantilever at only one end allows free bending of the whole cantilever.

A fiber-coupled diode laser was chosen for its high beam quality, small size, simplicity and low power consumption. The laser was set for a low operating power to accommodate the increasing operating current in response

Figure 3.2: Optical bench with the components marked. The cantilever was mounted beneath the baseplate (not visible in photo). The bread board is 18 x 11 cm and has a 12.5mm pitch

to the increasing temperature. The fiber ends in a collimator mounted on the breadboard. The collimator was adjusted to give a slightly converging beam to achieve a small spot size on the camera. The beam was sent via mirror M1 to the beamsplitter (BS) to generate two beams.

The beam path between splitting and combining the beams have equal path lengths to ensure equal sensitivity to cantilever bending. Mirrors M2, M3 and M4 are folding mirrors that bring the beams from the beamsplitter to both ends of the cantilever. A large beam separation of 60 mm was used to achieve a high sensitivity. By using a beam splitter to both split and combine the beams, the two beam paths fall on the same camera while having a large separation at the sample. One of the beams was given an out-of-plane offset to prevent overlapping beams on the camera. Both beams can travel the full length across the camera sensor without encountering other beams, providing a wide measurement range.

Mirror mounts M2 and M3 are Newport AG-M050N piezo-actuated mirror mounts (normal mounts are shown in figure 3.2). This allows remote control of the alignment of both beams when the setup is closed. The substrate must be a double-sided polished cantilever to allow the beams to be reflected off the backside. The substrate shields the two windows passing the beams in and out of the vessel from the deposition flux. A beam ex-

3. SELF-CONTAINED IN-VACUUM *in situ* THIN FILM STRESS MEASUREMENT TOOL

pander consisting of a -6 mm focal length lens (L1) and a 50mm focal length lens (L2) was installed to increase the sensitivity of the setup. Scanning the beams across the beam expander using the piezo mirror mount shows excellent linearity with only $\pm 0.5\%$ deviation. The resulting 0.5% uncertainty was considered negligible.

A Lumenera Lt425M-WOCG camera was chosen for its large sensor width of 11.3 mm and the absence of the cover glass of the CMOS sensor, eliminating fringes normally present due to a coherent source. It can capture 90 fps at the 4 megapixel resolution, allowing very fast processes to be captured even at high deposition rates.

When the setup is opened, the breadboard and sample remain in place; this allows the setup to stay aligned when the vessel is opened and closed for maintenance or to exchange either batteries or storage media. The piezo mirror mounts allow realignment after the vessel is closed, which can be used for compensating the deformation of the vessel when cycling from atmosphere to vacuum, and for realignment after changing samples without opening the vessel.

Measurement range and noise

The setup was designed to measure stress in multilayer systems such as a Mo/Si multilayer mirror. These typically have stress values of a several hundred MPa and a thickness of several hundred nanometers leading to a total force per unit width (F/w) of 100 N/m. Individual layers can have features in the stress development of 0.5 N/m occurring within 0.5 seconds. These features must be resolved from the noise.

The optical setup on the breadboard was made compact because of the limited available space. Due to this, the optical path from the cantilever to the camera is only 340 mm. The sensitivity was increased to the equivalent of a 2.1 m path length by using a beam expander. Propagation from the cantilever to the camera was calculated using ray transfer matrix analysis.

The measurement range using a 525 μm thick Si cantilever is 280 N/m with the beam staying in the center 75% width of the camera sensor to avoid clipping the beams, corresponding to a maximum radius of curvature of 30 meters. The beams have a FWHM of 1.4 mm or 250 pixels at the camera. This range is sufficient to capture a full multilayer stack. There are several ways in which the range can be increased or decreased for other applications. Thinner wafers decrease the range, which is suited for measuring a single or several thin layers. Thicker wafers can be used for thicker layers or systems. Reducing or increasing the magnification of the beam expander increases or decreases the range respectively.

The calculation of the sensitivity of the setup is only approximate as the path lengths have an uncertainty due to alignment. Calibration was performed by measuring the initial and final cantilever curvature *ex situ*

using a white light interferometer and matching the *in situ* measurement result to the *ex situ* measured curvature change.

Vibrations present in the system, such as the substrate movement over the magnetrons, were the main source of noise in the measurements. Typical measurement parameters are a 10 Hz acquisition rate, an 80 ms integration time and a 300 μm thick Si cantilever. The RMS noise measured for this configuration is 0.03 N/m. This is mostly due to oscillations present at much higher frequencies than the features in the stress development. A simple Gaussian moving average filter with a 1 Hz -3 dB point was found to be ideal to reduce noise while still resolving important features accurately. This filter effectively removes the noise that is due to the acceleration and deceleration of the substrate from magnetron to magnetron and reduces the noise to well below 0.01 N/m (shown in figure 3.7), corresponding to a 270 km radius of curvature.

The piezo mirror mounts can move the beam back onto the camera when the substrate curvature increases. This can extend the range to the point where Stoney's equation becomes non-linear. A 300 μm thick Si cantilever thickness was used in the measurements presented in this work, as this provided sufficiently low noise while having a large enough range to require few adjustments of the piezo mirror mounts.

3.2.3 Electronics

For the system to be fully standalone all the electronics needed to perform the measurement must be inside the vessel. The system must operate for the full duration of the deposition, which can take up to 10 hours for multilayers with over 200 periods, for example as used for 6.7 nm radiation. The opened vessel is shown in figure 3.3. A low power single board computer is used to read out the camera in order to save space and power consumption. A Fitlet iA10 single board computer with the heatsink option was chosen as this computer is rated to operate at 60 °C and has a build-in Wi-Fi adapter. It runs Debian Linux for stability, versatility and low overhead. The system is battery powered with two battery packs of total capacity 200 Wh. The measured power usage when idling was 10 W, while at a 10 Hz acquisition rate the usage was 13 W. The achieved runtime is over 12 hours, sufficient for the deposition of multilayers with over 200 periods.

3.2.4 Environment

Thermal

The only way for the setup to dissipate heat when in vacuum is by radiative heat transfer. Electronic components have limited operating temperatures, with the camera and laser diode being limited to 50 °C. This requires a low power dissipation in the setup to prevent overheating of the setup during a

3. SELF-CONTAINED IN-VACUUM *in situ* THIN FILM STRESS MEASUREMENT TOOL

Figure 3.3: An overview photo of the setup, showing (front to back) the laserdiode driver and thermocouple card, the Fitlet computer, optical breadboard and battery packs.

long deposition. The computer's CPU and the camera are fitted with extra heatsinking to prevent the CPU from throttling and to lower the noise level of the camera's CMOS sensor. A 4-channel thermocouple USB card from Phidgets Inc is included to measure temperatures inside the vessel and prevent overheating.

The temperature of the setup can be modelled by a simple thermal model:

$$dT/dt = \frac{P_e + P_{mag} - \epsilon\sigma A(T^4 - T_{chamber}^4)}{C} \quad (3.1)$$

where the input power consists of the electronic power usage P_e and the heat input from the magnetrons is denoted as P_{mag} . ϵ is the emissivity of the outside of the vessel and A the outside area; σ is the Stefan-Boltzmann constant; $T_{chamber}$ is the temperature of the process chamber and T the temperature of the vessel. The heat capacity of the system is denoted as C .

The electronic power usage is estimated by measuring the current drawn from the batteries and multiplying it by the battery voltage. The area of the vessel is approximately 0.3 m^2 . The heat input from the magnetrons, the emissivity and the heat capacity are derived from fitting the model to the measured vessel temperature. The magnetron deposition process deposits 5 W on average when depositing a Mo/Si multilayer. Depositing

a single period of a Mo/Si multilayer takes 167 seconds. The emissivity of the aluminum vessel is very low (around 0.15) and thus there is very little heat transfer by radiation. Due to its high heat capacity of 15 kJ/K the temperature of the vessel increases slowly. The vessel reached around 50 °C at the end of the 12 hour battery duration during which a 50 period Mo/Si multilayer was deposited.

Longer or higher power coatings require extra measures to prevent the operating temperature being exceeded. The temperature of the vessel, optical breadboard, computer heatsink and camera heatsink are monitored to prevent overheating. Better cooling can be achieved by applying a high emissivity coating on the vessel. An emissivity of 0.25 would be sufficient for continuous coating of Mo/Si periods.

Vibrations

Mechanical vibrations were the main source of noise in the measurement. The long cantilever behaves like a tuning fork and is particularly sensitive to its eigenfrequency and the harmonics of that. Avoiding overlap between vibrations present and the eigenfrequency is achieved by using a cantilever of a specific length. Combined with a long integration time that averages out vibrations, this resulted in a sufficiently low noise level.

Reducing the effect of vibrations can be improved by measuring the spectrum of the vibrations present. This allows choosing an optimum cantilever length. Choosing an integration period equal to a (sub)harmonic of the cantilever reduces the noise from oscillations of the cantilever. This was not done as the obtained noise performance was already more than adequate.

3.2.5 Communication

Control over the acquisition process and a realtime transfer of the measurement data allows verification of the performance of the setup and a realtime feedback loop of the deposition process. As the setup is fully self-contained, this requires wireless communication. A Wi-Fi connection was implemented to access the setup remotely and to transfer the camera images. An external computer performs the image processing to obtain the stress values and provides a live view of the stress development. This reduces the computation load of the setup but requires sufficient bandwidth to transfer the images. The setup continues independent of the external computer and saves the measurements locally in case the Wi-Fi connection or the external computer fails.

Both the vessel and the process chamber have an electrical feedthrough to which a short wire antenna was connected for the Wi-Fi communication. In case an electrical feedthrough is not available in the process chamber, placing the antenna in front of a viewport is also possible [20]. Both sides support the 802.11ac standard, giving a theoretical bandwidth of 433

Mbit/s. The connection was very reliable; a Wi-Fi connection could even be maintained in the sealed loadlock where no antenna was present. It is assumed that the viewport on the loadlock passes the signal in and out. The Wi-Fi connection was not influenced by the magnetron plasma from either the DC or the RF magnetrons. Substrate rotation of the whole setup at 1.5 Hz did not affect the connection either. Deposited material on the antenna did not noticeably affect the Wi-Fi performance.

Images of the full 4 megapixel resolution are approximately 200 kB after JPEG compression at a quality level of 90. This can increase to 270 kB as the system heats up and the camera noise level increases. A 1.5 MB/s download speed was obtained, transferring data from the setup to the Wi-Fi access point. However, this is only sufficient for an acquisition rate of 5 Hz.

An upload speed of 4.5 MB/s was achieved, demonstrating that sufficient bandwidth can be achieved. Proper antenna optimization and hardware choice should at least bring the download speed up to this level. The antenna length and geometry was not calculated or optimised, and this is most likely the reason for the low transfer rate. A 10 Hz rate used in figure 3.5, this was captured locally as the realtime feedback was not needed for the experiments performed. For this reason, no bandwidth saving measures, such as specifying a region of interest in the camera to exclude unused parts of the image, were taken.

3.3 Measurements

3.3.1 Acquisition

During measuring the stress, the camera continuously captures images and stores them in the JPEG format to conserve disk space and decrease the required bandwidth of the Wi-Fi connection. The acquired images are stored on a USB mass storage device connected to the Fitlet computer and are accessible via the Wi-Fi connection. The in-house written software has an 18 ms deadtime per image. This leads to a maximum acquisition rate of 50 Hz. As this is already sufficient to obtain sub-monolayer resolution for deposition rates of several nanometers per second, this was not further optimised. The deposition speeds used in this work are around 0.2 nm/s, making a 50 Hz rate unnecessary. A 10 Hz acquisition rate at a 80 ms integration time was chosen for most measurements, which still provides sub-monolayer resolution as well as a low noise due to the long integration time.

3.3.2 Processing

The live view calculated on the external computer calculates the center of mass of the beam profile on the images to determine their position. In addition, the full measurement data was processed after the measurement

Figure 3.4: Force per unit width recorded during a single period of a Mo/Si multilayer. This measurement has a 5 Hz acquisition rate at a 100 ms integration time

was finished using a 2D Gaussian fitting to determine the positions of the beam profiles more accurately. This calculation is not fast enough to be used for the live view in the current software implementation.

The beam position on the camera corresponds to the curvature. Stoney's equation, as shown in (2.1), is used to convert the curvature to the force per unit width. As explained in 2.3.2, the force per unit width (F/w) is defined as σh and used in this work.

3.3.3 Example measurements

To evaluate the performance of the metrology setup, *in situ* stress measurements were carried out during the deposition of a Mo/Si multilayer. The growth of Mo/Si is well characterized in the literature, and pioneering experiments on *in situ* stress have been reported[21], although those measurements were carried out without substrate movement or rotation.

In figure 3.4, the force per unit width recorded during a single period of a Mo/Si multilayer is shown. The as-deposited thicknesses are 3.5 nm for Mo and 4.5 nm for Si, typical for applications of these multilayers in XUV imaging applications. The multilayer stack is deposited onto a $\langle 100 \rangle$ Si

Figure 3.5: F/w of a 250 period MoSi deposition including a linear fit. The linear fit has an offset to avoid obscuring the data. The gap at 6000 seconds is an interruption in the data acquisition.

wafer. The first layer pair is therefore not deposited onto another Mo/Si period and has a different stress development (not shown).

The stress development of the coating reveals several interesting features. At 20 seconds, there is a tensile jump in the Mo stress after which the growth has changed from tensile to compressive. This is the transition from the amorphous phase to the polycrystalline phase which is known to occur around 2 nm[22, 23]. The Si stress development shows a very small tensile peak at 100 seconds. This is attributed to the end of the Molybdenum silicide interlayer formation and the start of pure Si growth[9, 24]. This silicide formation can be detrimental to the performance of a device, for example in case of an XUV Bragg multilayer mirror, the silicide reduces the refractive index contrast which lowers the reflectivity.

As discussed in section 3.2.2, by using the piezo actuated mirror mounts, a wide measurement range can be achieved. To evaluate the operation of the metrology device over many periods, a 250 period Mo/Si multilayer was deposited and the insitu stress measurements are shown in figures 3.5, 3.6 and 3.7. The results show a near constant stress per period over the full 250 period range. A linear fit to the data shows a quadratic residu with a $\pm 1\%$ deviation, which may be due to the non-linearity of Stoney's equation becoming significant as the total coating thickness is $1.75 \mu\text{m}$ on a $300 \mu\text{m}$

Figure 3.6: Magnification of indicated area of figure 3.5 showing 4 Mo/Si periods

Figure 3.7: Magnification of indicated area of figure 3.6 showing a 0.01 N/m noise level after a 1 Hz moving average filter was applied

thick cantilever. In addition, roughening of the multilayer can also influence growth in the tensile direction.

The heat input from the magnetrons also heats the substrate, typically by one to two °C after a single layer, leveling off to 10 °C during the normal deposition process. For thin coatings the cantilever can expand and contract without affecting the curvature. For thick coatings, the unequal thermal expansion of the cantilever and coating induces a curvature change. The resulting curvature change can be modeled and subtracted if needed.

3.4 Conclusions

We have developed a self-contained *in vacuum in situ* stress measurement setup which was mounted in a substrate holder in a UHV deposition system, while electrically and optically fully isolated from the deposition system. The stress setup was tested to be capable of measuring the thin film stress development during deposition at a 0.01 N/m RMS noise level. This sensitivity was more than sufficient to reveal small layer growth features in the stress development such as the phase transformation of molybdenum from amorphous to polycrystalline. A liveview of the stress development was implemented to monitor the stress realtime. The communication was achieved via a Wi-Fi connection.

The setup could, in principle, serve as a general *in vacuum* metrology platform. Extended measurement options such as a Faraday cup can be integrated as well as features such as sample heating or sample bias, which are generally challenging to implement for a substrate that moves and rotates in a vacuum chamber. The stand-alone nature of the system allows the integration of an extensive platform for metrology or sample interaction without extensive modification of the deposition chamber.

3.5 Acknowledgments

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Chapter 4

In situ studies of silicide formation during growth of molybdenum-silicon interfaces

Abstract

The growth development of nanometer thick Mo and Si layers was studied using *in situ* laser deflection and Low Energy Ion Scattering (LEIS). The growth stress obtained from changes in wafer curvature during growth is correlated to changes in the surface stoichiometry monitored by LEIS. For Si-on-Mo, the compressive-tensile-compressive stress development could be explained by the formation of interfacial silicide compounds and the transition between these and the bulk growth of Si. For Mo-on-Si, a strong initial tensile stress due to silicide formation saturates upon reduced availability of free Si at the growing Mo surface, followed by a near instantaneous tensile increase in stress related to the amorphous to crystalline phase transition, which coincides with the end of the compound formation, as determined with LEIS.

4.1 Introduction

Many current day nano-scale devices for electronic, mechanic and optical applications are based on nano-engineered structures of many layers with thicknesses in the order of a few nanometer or less. Interaction between these layers at the interfaces, including intermixing and formation of interface compounds, although sometimes useful (for example to improve adhesion), is in many cases detrimental to device performance. In particular the growth stress at interfaces, and related relaxation mechanisms, play an important role in device performance as they determine mechanical properties such as the tensile strength and lifetime (layer delamination)[1, 2].

In order to understand the complex relationship between layer growth and growth stress, precise metrology is required that is able to properly characterize and understand the layer growth processes, with emphasis on the processes that take place at the interfaces between thin films. In particular *in situ* metrology tools enable the analysis of complex systems as they evolve during deposition, rather than analyzing the resulting complex structure *ex situ*, where the individual effects of many synthesis steps may not be distinguishable anymore.

In this work we use *in situ* stress measurements to measure the intrinsic stress during layer deposition of nanometer thick bilayer systems. As an example system, Mo/Si was chosen. Mo/Si is an extensively studied material combination relevant for various optical and mechanical applications, and as such it is well known that Mo/Si interfaces play an important role[3, 4, 5], as well as the interface formation[6]. Mo is also investigated due to its phase transition being accessible at room temperature[7] and for its low mobility[8], which affects its growth mode and interface formation[9]. Mo_xSi_y compounds are also of interest, as the interface reactivity[10] and nucleation conditions[11] can be modified by this.

By using *in vacuo* Low Energy Ion Scattering (LEIS) we determine the composition of the outermost surface and correlate the results to the developing growth stresses, showing that the growth stresses that develop during deposition are intrinsically linked to the layered structure and in particular the formation of interfaces during growth.

4.2 Experimental

4.2.1 Layer deposition

All results presented here are obtained from thin films prepared in a high vacuum sputter deposition setup with a 10^{-8} base pressure, using DC magnetron sputtering with a 10^{-3} mbar argon working pressure. Movable magnetron targets of 100 mm diameter are placed underneath the substrate for normal incidence deposition. The target to substrate distance is 300 mm, the substrate is grounded and stationary. Samples were deposited onto

$\langle 100 \rangle$ Si wafer cantilever substrates of 80 x 10 mm, with deposition rates calibrated by *ex situ* x-ray reflectivity measurements on reference samples. A Mo deposition rate of 0.15 nm/s and a Si deposition rate of 0.27 nm/s was used. The magnetron voltages and powers were 340 V and 340 W for Mo and 470 V and 670 W for Si. All depositions were done at room temperature, the temperature rise of the cantilever during a separate deposition was measured by a thermocouple to be approximately 10 degree.

4.2.2 *In situ* stress measurement

Optical measurement techniques are regularly used to measure stress during deposition[12, 13, 14]. The *in situ* stress measurement is done by continuously measuring the curvature of a cantilever sample during the deposition process of the layers on the cantilever surface. The substrate curvature is measured using a dual laser beam deflectometer, where the beam position on the camera depends on the curvature of the cantilever which is influenced by the added stress during growth. As the typical deposition speed is around 0.2 nm/s and the acquisition frequency is 10 Hz, a subangstrom thickness resolution is achieved. This is small enough to distinguish effects within a fraction of a monolayer of deposited material. Due to the low noise level of 0.012 N/m these small features are still distinguishable.

Via Stoney's equation as shown in (2.1) the cantilever curvature is related to the force per unit width. The stress σ is related to the measured cantilever curvature κ via the coating thickness h . Processes such as compound formation and an amorphous-to-polycrystalline transition also induce a stress, however as the thickness of the material involved in these processes can be difficult to determine the force per unit width is used, defined as σh . This quantity is directly proportional to the measured cantilever curvature.

The derivative of the force per unit width curve is often assigned to the incremental growth stress of the newly added material, expressed in units of Pa. It should however be noted that this is strictly only possible in the absence of volumetric effects such as the occurrence of a phase transformation of the substrate layer during growth. In this work, the common procedure of taking the derivative of the force per unit width is applied, while specifically addressing volumetric changes where they occur. Intermittent starting and stopping of the deposition showed no relaxation effects.

The *in situ* stress measurement principle used is similar to ref. [15]. A fiber coupled laser with a 635 nm wavelength is used for easy visible alignment and a high beam quality, convenient in analyzing the camera images. The power per beam is below 1 mW, varying the power was found not to have an effect on the measurement. A beam splitter is used to generate two beams and combine them to capture their position on a single camera. The two laser beams are spaced 50mm apart on the cantilever and reflect off the cantilever surface. The cantilever is clamped on only one side to avoid forces on the cantilever that would influence its curvature.

By taking the difference in deflection of the two beams, the measurement is sensitive to the change in curvature of the cantilever in between the two beams, eliminating contributions from e.g. clamping effects. The path length from the laser to the cantilever is approximately 1 m, after which the beams are reflected back close to the cantilever, reflecting off the cantilever a second time to double the sensitivity. The beam then follow the same 1 m long path back until the beamsplitter reflects them to the camera. The stress measured using the *in situ* deflectometer setup was calibrated *ex situ* by measuring the cantilever curvature before and after deposition using a white light interferometer.

4.2.3 LEIS measurement

LEIS measurements were performed in a Qtac¹⁰⁰ instrument manufactured by IONTOF, in an UHV chamber with base pressure around 1×10^{-10} mbar. The incident ion beam is 3 keV He⁺ with normal incidence on the sample surface. A double toroidal energy analyzer accepts ions with a scattering angle of 145°, using an azimuthal acceptance angle of 360° for an efficient collection. The ion energy after scattering from a given surface atom depends on the mass ratio of the ion and the surface atom. The high surface sensitivity of LEIS originates in the very high neutralization probability of scattered ions as the ion-surface interaction is much longer for ions scattered from buried atomic layers, and therefore the neutralization probability for those ions is close to 1 [16, 17, 18, 19]. Projectiles scattered from buried layers lose additional energy proportional to the travel length, and can be detected if they reionize upon escaping the sample surface. The signal from these ions is therefore separated in both intensity and energy from the signal from surface ions [16].

The surface composition was quantified according to the method described in ref. [16]. First, integral peak areas were obtained by fitting a Gaussian to Si or O peaks. Only the high-energy side of the Mo peak was used for fitting due to interference of the intense tail at the low-energy side. Then, to calculate surface coverages of Mo and Si, integrated intensities S_i of their LEIS surface peaks for each spectrum were divided by intensities of reference samples, for which pure sputter-cleaned Mo and Si surfaces were chosen ($S_{\text{Mo}}^{\text{ref}} = 17280$ counts/nC and $S_{\text{Si}}^{\text{ref}} = 3740$ counts/nC). Next, surface atomic densities (SAD) N_i of Mo and Si were calculated as

$$N_i = N_i^{\text{ref}} \frac{S_i}{S_i^{\text{ref}}}. \quad (4.1)$$

The surface atomic densities of the reference samples N_i^{ref} were calculated from the bulk mass densities ρ_i in the following way [16]:

$$N_i^{\text{ref}} \approx \left(\frac{\rho_i N_{\text{Av}}}{M_i} \right)^{\frac{2}{3}}, \quad (4.2)$$

Material	SAD ($10^{19} \text{ atoms/m}^2$)
Mo	1.60
MoSi ₂	1.78
Mo ₅ Si ₃	1.70
Si	1.36

Table 4.1: SAD's used in this work

where N_{Av} is Avogadro's number and M_i is the molar mass. We obtain $N_{\text{Mo}}^{\text{ref}} = 1.55 \times 10^{-19}$ and $N_{\text{Si}}^{\text{ref}} = 1.31 \times 10^{-19}$ atoms/m². The accuracy of the values of SAD's obtained this way depends on the validity of equation 4.2 for each reference sample, which means that values of SAD's contain an unknown scaling factor, constant for each element. In this paper we therefore only compare relative changes of SAD's. The values of $S_{\text{O}}^{\text{ref}}$ and $N_{\text{O}}^{\text{ref}}$ for trace amounts of O contamination were taken from [20].

The SAD's used in this work are included in table 4.1. The SAD's of compounds and mixtures are the total number of atoms at the surface, regardless of their species. A simple mixture is expected to have a SAD inbetween the SAD's of its constituent atoms, for a dense compound it is expected to be higher.

The LEIS measurements were performed for incremental thicknesses of top layers, which allows to combine the results in a so-called deposition depth profile (in contrast to a sputter depth profile). To reduce the effect of surface contamination during LEIS analysis, for each film thickness a dedicated sample was made in a separate magnetron sputter deposition chamber and transferred in-vacuum to the LEIS setup within 10-15 minutes after deposition. This procedure allowed to keep oxygen content on the surface lower than 5% for most samples, with an exception of Mo films without Si, for which atomic fraction of O reaches 10%.

As LEIS measurements are not sensitive to the phase of the material (amorphous or polycrystalline) it cannot be concluded from them what the phase of the layers, interfaces or compounds formed is. Only for Mo layers the amorphous-to-polycrystalline phase transition was observed, using XRD.

4.3 Measurement results

4.3.1 Si on Mo Growth

Raw LEIS spectra for Mo-on-Si and Si-on-Mo growth are shown in figures 4.1A and 4.1B. Figure 4.2 shows the stress that is measured during growth of Si onto Mo, as measured in N/m (A) and the derivative in GPa (B). Analyzed LEIS data during Si-on-Mo growth are shown in the bottom graph (C).

4. *In situ* STUDIES OF SILICIDE FORMATION DURING GROWTH OF MOLYBDENUM-SILICON INTERFACES

Figure 4.1: a) 3 keV He^+ scattering spectra of a) Mo on Si and b) Si on Mo. The thickness of the top film is shown to label each spectrum. Positions of surface peaks of Mo and Si are indicated.

In general, a predominantly strong compressive stress is observed during Si layer growth, consistent with earlier work [21, 22]. The *in situ* metrology reveals several additional details as seen in figure 4.2B. Several features can be observed in the stress development. A small tensile peak of 0.1 N/m is visible within the first 0.15 nm, indicated by the first vertical dotted line in figure 4.2. A compressive stress of -5 GPa is observed after the initial 0.15 nm. The compressive stress reduces with increasing Si growth, resulting in a tensile stress around 1.3 nm of deposited Si, indicated by the second vertical dotted line figure 4.2. At 1.6 nm (indicated by the third vertical line in figure 4.2B) the stress has settled to -1.1 GPa (indicated by the lower horizontal line) and remains constant for the rest of the layer thickness.

The LEIS results in figure 4.2 show a monotonic increase of Si coverage and monotonic decrease of Mo coverage. The total SAD monotonically decreases from the bulk Mo value to the bulk Si value, which it reaches after 1.3 nm of Si deposited.

The XY plot of the Mo SAD and Si SAD in figure 4.3A shows how far the SAD's deviate from a theoretical simple mixture of the two. The blue line indicates the convex combination (CC) of the Mo and Si SAD corresponding to the case of a simple mixed coverage. A convex combination is a linear combination with all weights equal or larger than zero, and with the sum of the weights equal to one. The red line is the experimental data and shows the combined Mo and Si SAD progressing from bulk Mo to bulk Si.

From the start of the Si deposition up to 0.5 nm of Si deposited the combined SAD is increasing compared to the CC. After 0.5 nm the combined SAD decreases and converges to the bulk Si value, reaching it at 1.3 nm Si deposited.

Figure 4.2: Si on Mo: A) Stress development in N/m as measured, B) The derivative of the stress development in GPa, C) LEIS SAD's

Figure 4.3: LEIS Si vs Mo surface atomic density (SAD) for A) Si on Mo growth, and B) Mo on Si growth. A positive deviation from the linear line indicates the total SAD is higher than a mixed of the coverage of both, indicating compound formation.

Figure 4.4: Mo on Si: A) Stress development in N/m as measured, B) The derivative of the stress development in GPa, C) LEIS SAD's

4.3.2 Mo on Si growth

Figure 4.4 shows the stress that is measured during growth of Si onto Mo, as measured in N/m (A) and the derivative in GPa (B). The LEIS data during Si-on-Mo growth is shown in the bottom graph (C).

The initial stress is strongly tensile at 5 GPa. The tensile stress levels off with the Mo growth towards a compressive growth, reaching 0 GPa around 1.8 nm. At 2.1 a sharp tensile step of 0.7 N/m occurs, after which the growth is compressive at approximately 1 GPa.

The LEIS measurement shows the SAD of Si and Mo change slower than for the Si on Mo case. The Si SAD only reaches 0 after 3 nm of Mo deposited. The total SAD does not increase monotonically from the bulk Si value to the bulk Mo value.

Similar to Si on Mo, the combined SAD does not follow the CC from pure Mo to pure Si as can be observed in figure 4.3 (B). For up to 2 nm of Mo deposited the combined Mo and Si SAD is increasingly higher (indicated in red) than the CC (indicated in blue) of Mo and Si.

4.4 Discussion

4.4.1 Growth mode

During magnetron sputter deposition, adatom energies are typically of the order of a few eV to a few tens of eV, sufficient to break bonds at the substrate surface and enabling the formation of Si-Mo bonds during interface growth. When the substrate is near room temperature, the low mobility per adatom results in a stochastic growth mode, leading to amorphous and/or polycrystalline film growth. The adatom energies during sputtering are sufficiently high to densify the growing layer and create a smooth adlayer with a low roughness. The roughnesses of Mo/Si systems in the deposition setup used are typically in the order of 0.2 nm RMS, determined by AFM measurement. Finally, the large negative enthalpy of mixing of Mo and Si [23] shows that island formation due to segregation should not occur. This excludes large scale island formation typically seen in Volmer Weber growth, as this would result in a significantly larger roughness than observed. The low mobility and amorphous growth also excludes Stranski-Krastanov growth.

Surface morphology and roughness affects the LEIS signal as well, reducing it by a certain roughness factor R due to blocking and shadowing of ions by features located higher than them [16]. This effect is non-conventional – the roughness factor does not depend on the absolute height of features, but instead on their angle, which means that even atomic scale disorder can play a role [18]. Since exact atomic scale arrangement of atoms for our surfaces is unknown, the value of roughness factor also remains unknown but lower than unity (we can expect it to be around 0.8 for polycrystalline metal [18]). Without additional information we have to assume it to be constant.

Even if the assumption is wrong, one can argue that the increase of the sum of the SAD of Mo and Si, as observed in figure 4.3, cannot be explained by a roughness factor. For example, in intermediate stages of growth of Mo on crystalline Si substrates roughness increases [24], and the appearance of extra step edges should lead to a decrease of LEIS signal. However, the opposite is observed in figure 4.3. As such we explain this effect by compound formation, and potential changes in roughness would only mean the effect of compound formation is even stronger.

4.4.2 Si on Mo Growth

The initial tensile peak, indicated in figure 4.2A by the vertical line at 0.15 nm, corresponds to a submonolayer coverage, indicating that the tensile peak is due to a quickly saturating effect. According to the LEIS measurements, the SAD's change only slowly, i.e. on a nanometer scale, suggesting strong intermixing. The submonolayer equivalent tensile stress is therefore not related to the nanometer scale intermixing. Surface stress effects due

to island formation, such as treated in ref. [25], do not occur due to the stochastic growth mode. In addition any significant island formation would result in a substantial change in surface coverage which is not observed in the submonolayer regime. The first submonolayer of Si atoms may actually diffuse into the Mo grain boundaries and may introduce a tensile stress as the Si atoms fill voids that are too small for Mo atoms and act as a cohesive force between grains.

The compressive stress following after the tensile peak is attributed to compound formation of the arriving Si with the Mo layer. The more mobile Si atoms diffuse into and expand the Mo layer when creating a compound, creating a compressive stress. This process depends on the accessibility of Mo, therefore the compressive stress due to compound formation and the availability of Mo on the surface are proportional. Both the compressive stress and the Mo SAD decrease as visible in figure 4.2B and 4.2C, where after 1.3 nm of deposited Si the Mo SAD reaches zero and the Si incremental growth stress reaches a maximum.

Figure 4.3A shows the Mo SAD plotted as a function of the Si SAD. The covering of Mo with Si without any interaction of the two would be a convex combination of the Mo and Si SAD's as indicated by the blue line. However, the combined SAD of Mo and Si is higher, up to a 20% increase at 0.5 nm. This is a clear indication of compound formation, where for all known molybdenum silicides the compound density is much higher than a convex combination of the element densities. This compound formation apparently takes place in particular in the first 0.5 nm Si deposited. After 0.5 nm, the SAD converges to the Si SAD, indicating reduced or no compound formation and additional elemental Si slowly covering the interface compound, until around 1.5 nm where no Mo is present at the surface and bulk Si growth is starting.

The compounds formed during Si on Mo growth depend mainly on the availability of Mo and Si[26]. According to the SAD's as measured by LEIS, the effective stoichiometry at the surface in the first 0.5 nm, where an abundance of Mo is present, can be expected to be close to Mo_3Si_2 and/or Mo_5Si_3 . Mo_3Si_2 has not been reported in literature for Mo/Si systems, so this compound is not considered. For surface coverages above 0.5 nm, much more Si rich stoichiometries are observed at the surface, suggesting either coexistence of Si and Mo_5Si_3 , or the formation of MoSi_2 . Since MoSi_2 has an even higher SAD than Mo_5Si_3 , any significant formation of MoSi_2 would have shown a *further* increase in the combined SAD past 0.5 nm. Since the interface formation occurs mainly in the first 0.5 nm the abundance of Mo most likely gives rise to Mo_5Si_3 compound formation as reported by Zoethout et. al.[6]. Estimating the interface width from the LEIS measurement using the method also used by Coloma Ribera et. al.[20] results in a σ of 0.4 nm, similar to what is found in literature[27].

Both the Mo_5Si_3 formation at the start of the Si deposition and the bulk Si growth after about 1.5 nm show compressive growth stresses. However,

in-between these two growth regimes, around 1.3 nm of deposited Si (indicated in figure 4.2 by a vertical line), a tensile stress occurs. The SAD's change monotonically and therefore the compressive-tensile-compressive behavior cannot be explained by processes only depending on the availability of material at the surface, as this would result in a stress development that would be proportional to the SAD's.

Instead, the compressive-tensile-compressive growth indicates that the transition from Mo_5Si_3 formation to bulk Si growth is not gradual but shows a tensile interface contribution from the $\text{Mo}_5\text{Si}_3/\text{Si}$ interface. As the Mo SAD decreases more and more of the surface consists of Mo_5Si_3 and the Mo layer is no longer accessible, stopping the Mo_5Si_3 formation. The arriving Si atoms now intermix with Mo_5Si_3 with which the Si cannot form a covalent bond. This causes many dangling bonds in the Si due to this interface, resulting in a tensile stress. This is similar to porous Si, where the atoms sit further apart and therefore have more dangling bonds, which also results in a tensile stress. This tensile component is therefore proportional to the Mo_5Si_3 present on the surface which has a maximum after the Mo_5Si_3 interlayer has formed but before the bulk Si layer forms on top of it.

In other work a subsurface interface formation around 1 nm of deposited Si in a Si-on-Mo system is suggested[6], which could also explain a tensile stress due to compaction of the subsurface layer. It would not be visible in the LEIS measurement as the change is subsurface which not register on the LEIS signal. However, in this study subsurface interface formation is not considered as a cause for tensile stress due to the fact that a similar broad tensile peak was observed when depositing Si onto a SiO_2 layer, suggesting that the tensile peak is not due to subsurface interface formation effects but due to formation of a Si/inert surface interface, e.g. Si on Mo_5Si_3 or Si on SiO_2 .

After 1.3 nm of Si deposited the LEIS data shows a pure Si surface. At 1.6 nm (indicated in figure 4.2 by a vertical line), the Mo presence is no longer influencing the stress of the newly added material at the surface, clearly demonstrating that interface effects were the cause of the non-linear stress behavior observed in Si-on-Mo growth. The constant stress of -1.1 GPa from this point onwards (indicated in figure 4.2 by a horizontal line) indicates the bulk growth starts at this point. This compressive stress depends on the specific growth conditions, where in the case of magnetron sputtering ad-atoms arriving with significant energy densify the layer by a peening effect[28, 29] and create compressive stress.

4.4.3 Mo on Si growth

The initial stress is strongly tensile at 5 GPa, which is consistent with what is reported elsewhere in literature[8, 10, 21]. The interface formed is reported to be MoSi_2 [6, 21], agreeing with the abundance of Si on the surface

favoring MoSi_2 [26]. This initial tensile stress was found to decrease strongly when the underlying Si layer is prevented to form MoSi_2 , for example due to the presence of a several angstrom interlayer or passivation (both with no significant contribution to the stress themselves), indicating that the tensile stress is mainly due to compound formation and not due to surface stress.

In contrast to Mo_5Si_3 formation for the case of Si on Mo, where Si atoms moving into the existing surface create a compressive stress, the addition of Mo on a surface allows the Si atoms to move out of the surface to form a compound [24]. The voids left by Si when moving to the Mo on top to form a compound introduce tensile stress.

The tensile stress reduces with Mo growth, effectively being limited to the availability of free Si at the surface to form MoSi_2 , consistent with the changes in SAD's as observed in the LEIS data. Note that the intermixing range is much larger for Mo on Si as compared to Si on Mo, which in literature is often attributed to difference in crystallinity[9], cohesion[30] and ad-atom-substrate interaction strength[31]. Estimating the interface width from the LEIS measurement using the method also used by Coloma Ribera et. al.[20] results in a σ of 1.0 nm, similar to what is found in literature[27].

Figure 4.3B shows the Mo SAD plotted as a function of the Si SAD. The combined SAD is higher than what would be expected by the simple covering of the Si layer by a Mo layer (represented by the blue line). This indicates compound formation occurs up to 2 nm, which coincides with the amorphous to polycrystalline transition. observed in the *in situ* stress measurement. After 2 nm, the combined SAD reduces, indicating the covering of the Mo_xSi_y compound with Mo, and reaching the value of a convex combination of Mo and Si at 2.7 nm. From 2.7 nm, the combined SAD remains a convex combination of Mo and Si, indicating no compound present at the surface, but there is still Si present at the surface according to LEIS. This may be due to Si which segregates onto the surface without actually forming a compound.

As the Si availability drops, as shown in the LEIS measurements, the stress slowly reduces to a stress free growth. Continued growth would actually become compressive as shown by Fillon et. al.[10] if crystallization would be prohibited. However, at 2.1 nm a sharp tensile step of 0.7 N/m is visible. XRD measurements done confirmed that this is the phase transformation of the Mo layer from amorphous to polycrystalline, in line with what is reported in literature[7, 10]. The phase transformation compacts the Mo layer as the crystallites have a denser packing of the atoms. This volume decrease can relax in the out of plane direction during growth, but still induces a strong tensile stress in the in-plane direction, causing the tensile step.

After the crystallization the stress is expected to be mainly determined by the growth of the crystallites and the grain boundaries. The observed compressive stress may be due to overfilling of the grain boundaries. For

increasing thicknesses the roughness increases and the competition between the growing grains can lead to voids, which would introduce a tensile contribution. The evolution of the grains in size and grain boundary density depends strongly on the initial polycrystalline texture, which is also influenced by impurities.

4.5 Conclusions

The growth of Si on Mo and Mo on Si has been investigated with *in situ* stress and LEIS. The Si growth shows a compressive-tensile-compressive behavior, where added compressive stress from the initial, presumed Mo_5Si_3 interlayer formation is proportional with the Mo availability on the surface. This compressive stress is followed by a tensile $\text{Mo}_5\text{Si}_3/\text{Si}$ interface that has many Si dangling bonds due to the inert Mo_5Si_3 and this tensile stress component reduces with Mo_5Si_3 availability on the surface. Finally, Si bulk growth starts at 1.5 nm deposited Si and shows a compressive stress of 1.1 GPa due to peening.

For Mo, a thick MoSi_2 interface is formed that shows strong tensile stress due to defects created in the Si surface upon MoSi_2 formation. This tensile stress slowly reduces due to reduced availability of Si. A strong tensile stress is observed at 2.1 nm, exactly at the amorphous to polycrystalline phase transition.

For both Si on Mo and Mo on Si, the LEIS data clearly shows that the combined SAD's during interface growth are much higher than a convex combination of the Mo and Si SAD's, clear evidence of high density compound formation. The exact point where compound formation stops and additional deposited material remains elemental is clearly observed.

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Chapter 5

In situ study of Mo growth on a-Si with C and Ru interlayers

Abstract

The stress development during Mo growth on an amorphous Si substrate layer is studied by *in situ* measurement of the intrinsic growth stress. The effect of interlayers between Si and Mo is investigated using interlayers of C and Ru, representing surfaces with small, mobile atoms (C) and large immobile atoms (Ru), leading to low and high diffusivity into Mo. The results show a strong influence of interlayers on the Mo stress development and the thickness at which the amorphous-to-polycrystalline transition occurs in the Mo. In particular the tensile stress of the initial growth decreases for both interlayers and the transition occurs earlier when using a Ru interlayer and later when using a C interlayer.

5.1 Introduction

Thin metal films have a wide range of applications, for example in microelectronics and microelectromechanical systems (MEMS). As the intrinsic growth stress and structure is important for the systems performance, the thin film growth process has been studied extensively[1, 2, 3].

Low mobility metals such as Mo, W and Ta have a 2D growth mode at room temperature. This allows the growth of low roughness films, where morphological effects such as island coalescence are absent. In this growth mode, the substrate-film interface that is formed during growth will play a major role in determining the film structure, including film stress and film crystallinity. In case of Mo and W, a tensile step is visible in the stress evolution due to the phase transformation from amorphous to polycrystalline [4]. This phase transformation is accessible at room temperature growth, and may reveal essential material properties. The mechanism of this phase transformation is attributed to a balance between two driving forces. The bulk force drives towards a (poly-)crystalline phase, as for a bulk material this is the energetically favorable state. The interfaces (the Mo on Si interface and the vacuum to Mo interface) stabilize the amorphous phase, which creates a balance between the two depending on the layer thickness[5, 6, 7].

In this work we focus on the growth of Mo on amorphous Si (a-Si), a commonly used system to study low mobility metals[4, 5, 8]. In order to study the Mo stress development dependence on the interface and the interaction with the substrate, the interface properties are modified by the addition of C or Ru interlayers of increasing thickness between a-Si and Mo. The effect of such angstrom thin interlayers on growth stresses in Mo is investigated by wafer bow measurements during the film growth.

In order to study the Mo during growth, a continuous *in situ* measurement technique is needed, as *ex situ* measurements can only analyse the end result of processes, such as diffusion and compound formation. The intrinsic stress of thin films depends on various physical effects, such as the layer structure and composition. Stress, therefore, is an important means to analyse the Mo growth. *In situ* measurements can reveal important growth properties and processes that would otherwise remain hidden.

C and Ru are chosen as interlayer materials, both well studied[9, 10, 11, 12]. Carbon represents a class of small atoms, with expected high diffusivity in Mo[13], whereas larger atoms, such as the periodic system neighboring 3d-metal ruthenium, may be expected to show no strong interaction with Mo.

5.2 Experimental

Thin films of Mo, C, and Ru were grown using DC magnetron sputtering at a 10^{-3} argon working pressure with a 10^{-8} background pressure. The

deposition rates were in the order of 0.1 nm/s and are calibrated beforehand by *ex situ* x-ray reflectivity measurements on reference samples. Films were deposited onto 10 x 80 mm cantilevers that are cut from a $\langle 100 \rangle$ Si wafer.

The stress during film growth is determined using a dual beam laser deflectometer, which measures the curvature of the silicon cantilever during the layer deposition. An *ex situ* calibration of the cantilever curvature measurement is performed using a White Light Interferometer (WLI). A Mo deposition rate of 0.2 nm/s, together with a curvature measurement data acquisition rate of 10 Hz, results in a sub-monolayer thickness resolution of the stress measurement. A noise level of 0.03 N/m RMS is achieved, allowing small stress changes to be resolved.

The deposition rates are calibrated beforehand by *ex situ* x-ray reflectivity measurements on reference samples.

The curvature of the cantilever is related to the force per unit width via Stoney's equation, as shown in (2.1). The force per unit width, defined as σh , is used in this work since it is directly proportional to the curvature measured. The derivative of the curve is the incremental stress, which can only be associated with layer growth stress when there are no effects that arise due to modification of the underlying structure, such as compound formation or crystallization.

The modification of the interface is done gradually by repeating the deposition and measurement of the system, for interlayer thicknesses from 0 nm to 1 nm in 0.1 nm steps, revealing the effect of an increasingly thicker interlayer to the stress development of Mo.

5.3 Results and Discussion

Mo on a-Si substrate

Figure 5.1 shows the force per unit width (F/w), measured during Mo growth on a-Si. The growth of Mo has a high initial tensile stress due to MoSi_2 formation as the more mobile Si diffuses into the Mo, leaving tensile voids[14]. In order to quantify the interaction of the first Mo monolayer (approximately 0.3 nm Mo thick) with the substrate, a linear fit is made in this region of the stress evolution, illustrated in figure 5.1. The first 0.1 nm of the deposition is excluded to avoid any artefacts of the start of the deposition.

The slope of the F/w curve during the first monolayer of Mo growth corresponds to a tensile stress of 5 GPa, which reduces with increasing Mo thickness. This reduction in tensile stress can be linked to the Mo/Si compound formation, which reduces with the thickness deposited due to the reduced availability of Si at the surface. Due to the strong intermixing of Mo and Si (up to 2 nm[ref]), the tensile stress reduces only slowly and would develop into the bulk compressive stress typical for sputter deposited amorphous materials[8]. Before this compressive growth sets in,

Figure 5.1: Stress evolution of 6 nm Mo on a-Si. Two linear fits are shown in red for the initial stress (0.1-0.3 nm interval) and the post-crystallization stress (0.5 nm interval after crystallization)

an amorphous-to-polycrystalline transition occurs at 2.2 nm, which is confirmed by XRD measurements. This phase transition is visible as a 0.7 N/m step in the stress evolution.

The stress after this crystallization is most likely determined by the growth of the grains and interaction of them at their grain boundaries. The stress after crystallization (determined by a linear fit through the first 0.5 nm after crystallization, illustrated in figure 5.1) is compressive at 1.5 GPa but drops to 0 GPa at 4.5 nm after which it becomes tensile. XRD measurements performed show that the grain growth of polycrystalline Mo changes from isotropic growth in the first 3 nm to columnar growth, similar to what is seen in literature[15]. The competition between grains may therefore result in a compressive stress while the columnar growth mode relaxes to a tensile growth stress due to underdense grain boundaries[16].

Mo on C interlayer

Figure 5.2 shows the stress evolution of a Mo layer, as deposited on an a-Si substrate with C interlayers of varying thickness. The presence of a C interlayer, even in case of only 0.1 nm thickness, has a strong impact on the stress evolution.

From the graph it is apparent that the largest changes in stress appear in the first monolayer of Mo growth, where the interaction between Mo and C on a-Si plays an important role. To quantify this interaction, a linear fit to the data has been performed in the first monolayer of growth. The resulting Mo initial growth stress versus the C interlayer thickness is plotted in figure 5.3.

Figure 5.2: Stress evolution of Mo growth on a C interlayer on an a-Si substrate. From bottom to top the C thickness increases from 0.0 nm to 1.0 nm with 0.1nm steps. The amorphous-to-polycrystalline transitions are indicated by red dots which are connected to visualise the shift, therefore the growth left of the red line is amorphous and poly-crystalline right of the line.

Figure 5.3: The stress of the first monolayer of Mo growth (linear fit in 0.1-0.3 nm interval), as a function of C or Ru interlayer thickness.

Figure 5.4: Thickness of Mo at the point of crystallization depending on interlayer thickness

Without a C interlayer, the initial Mo stress is 5 GPa. This stress strongly reduces to about 2 GPa for a 0.2 nm C interlayer and remains approximately constant for thicker interlayers. Such a large stress change occurring within the first monolayer indicates this is an interface effect. The stress reduction at the interface due to only 0.2 nm C suggests the C interlayer intermixes only little with the a-Si substrate and provides a nearly closed layer that reduces the interaction of Mo with the a-Si substrate. The residual tensile stress for thick C layers may be due to MoC compound formation.

Besides the large change of stress of the interface region, there are several other changes in the Mo growth due to the C interlayer. Most prominent is the effect on the thickness at which Mo crystallizes. Figure 5.4 shows the crystallization thickness for Mo as a function of the C interlayer thickness. The crystallization thickness increases almost linearly with increasing C thickness, suggesting that the entire C interlayer contributes to the delayed crystallization by intermixing with the Mo.

This is in line with the observation of Nedelcu et. al. that C diffuses strongly through Mo[13]. The C presence in Mo reduces the bulk driving force towards crystallization, which delays the phase transition[8]. The diffusion is apparently strong enough to influence the stress evolution even *after* the phase transition has taken place, as the stress evolution after crystallization has become linear and more compressive for all interlayer thicknesses, as observed in figure 5.2. As the linear stress evolution is present for all interlayer thicknesses including 0.1 nm, it is not a bulk effect, as this would be proportional to the amount of C present inside the Mo. The compressive stress may be due to the C atoms filling the grain boundaries, removing the tensile contribution of underdense grain boundaries, leading to a continuous compressive bulk growth.

Mo on Ru interlayer

Figure 5.5 shows the stress evolution of a Mo layer, as deposited on an a-Si substrate with Ru interlayers of varying thickness. Similar to the case for Mo on C, the stress in the first monolayer of Mo growth on Ru has been plotted in figure 5.3. The 5 GPa tensile stress in the first 0.3 nm reduces with increasing Ru layer thickness, saturating at 0.5 GPa for a 0.7 nm Ru interlayer. Unlike C, Ru intermixes strongly with a-Si[11, 13]. It is unlikely that the Ru forms a silicide compound that prevents MoSi₂ formation already at 0.1 nm. However, it may prevent the process of tensile void formation by the Mo (possibly this process may already occur during the interlayer deposition), reducing the stress of the initial MoSi₂ formation. As both C and Ru prevent MoSi₂ formation, the initial tensile stress drops for both interlayers used. However, due to the stronger intermixing of Ru with the a-Si layer, this reduction saturates at higher thicknesses of Mo deposited than for the C interlayer case.

Figure 5.5: The stress evolution of Mo layers grown on a Ru interlayer of increasing thickness on an a-Si substrate. From bottom to top the Ru thickness ranges from 0.0 nm to 1.0 nm in 0.1nm steps. The amorphous-to-polycrystalline transitions are indicated by red dots which are connected to visualise the shift of the transition to smaller Mo thickness with increasing Ru interlayer thickness.

Figure 5.6: Mo on a-Si (blue) and Mo on 1 nm Ru on a-Si (red), plotted with a 0.7 nm and 2.8 N/m offset

It is observed that the thickness for Mo crystallization is also affected by the Ru interlayer, although in a different way than using C interlayers. The deposited thickness required for Mo crystallization reduces when the Ru interlayer is thicker, as shown in Figure 5.4. Up to around 0.5 nm Ru deposited, there is an approximately 1:1 inverse linear relation between change in the thickness required for crystallization and the Ru interlayer thickness, indicated by the black dashed line, i.e. for every angstrom of Ru deposited one angstrom of Mo less is required to reach the phase transition point. The combined thickness of the Ru interlayer and the Mo deposited until the phase transition point is reached is constant in this region and independent of the Ru interlayer thickness. This may indicate the Ru_xSi_y interface not only consumes Si and prevents Mo_xSi_y formation, but also acts as a virtually identical template to MoSi_2 for Mo growth. After 0.5 nm, the reduction in crystallization thickness saturates, indicating that the Ru is not a perfect template and that the differences between Ru and Mo become significant.

In order to study the templating behavior of Mo on Ru on a-Si, the stress development of Mo on a-Si and Mo on 1 nm Ru interlayer on a-Si are plotted in figure 5.6. The stress evolution of Mo on 1 nm Ru is remarkably similar to that of Mo on a-Si layer growth at a later growth stage; in fact a near perfect match between data is obtained when the Mo on Ru interlayer on a-Si data is offset by 0.7 nm, confirming the templating behavior. For a perfect templating behavior (all properties of Ru being equal to Mo), the

stress evolution of Mo on 1 nm Ru would be equal to the Mo stress evolution from 1 nm onwards. However, the templating behavior is not perfect, as the offset is only 0.7 nm. Interestingly, the onset of the phase transformation is reduced by 0.5 nm (figure 5.4), which is less than the "templating" shift of 0.7 nm.

The templating behavior of Ru for Mo is likely due to similar chemical reactivity of Ru and Mo to form silicides. Both Ru and Mo silicides have similar properties regarding surface free energy and reactivity, providing an inert surface for Mo to grow on. This is in line with the 1:1 inverse linear relation of the interlayer thickness and crystallization shift. It is expected that, past the interface formation, the difference between Ru and Mo becomes apparent and the templating behavior decreases. Therefore it is expected that for larger thicknesses (past the interface formation) the templating behavior reduces. The templating affects the stress and phase transformation differently, likely due to the similarities of the amorphous phase but the different driving force towards crystallization, highlighted by the different lattices of Mo and Ru (BCC and HCP, respectively).

The stress development after crystallization for thin (a few angstrom) Ru interlayers is similar to Mo on a-Si, visible in the lowest two plots in figure 5.5 (in contrast to Mo on C interlayer on a-Si, as shown in the bottom two plots in figure 5.2). The stress after the transition becomes less compressive and turns to tensile earlier for increasing interlayer thickness. Similar to the templating behavior that resulted in an earlier phase transition, the Ru interlayer may also result in an earlier change to tensile growth. The grain size evolution and the resulting stress may be strongly influenced by the initial grain size and strain. The reduced intermixing of Si with Mo due to the interlayer may therefore result in a large change in the stress evolution after crystallization. For a Mo on Ru interlayer deposition only minor intermixing (sputter induced) is expected. This in contrast to the Mo on C interlayer on a-Si, where the C interlayer diffuses not significantly into the a-Si but mainly into the Mo and postpones the crystallization.

5.4 Conclusions

The stress development of Mo during growth on a-Si has been studied using *in situ* stress measurement by using different interlayers between the Mo and Si. Both C and Ru interlayers reduce the Mo/Si intermixing and reduce the initial tensile stress development that is associated with voids created in Si during Mo_xSi_y formation. The C interlayer strongly intermixes with the Mo layer, postponing the crystallization and modifying the crystalline structure. The Ru interlayer forms a thick RuSi interface that acts as a template similar to MoSi, providing a favorable interface for Mo to crystallize earlier, compared to the case for C.

These results show that diffusion of substrate and interlayer atoms into a

growing layer can play an important role in the growth of metal adlayers. In particular the atomic species of the interlayer can be of critical importance for the strain development and crystallization behavior.

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Chapter 6

In situ X-ray study of the amorphous to poly-crystalline transition of thin film Mo

6.1 Introduction

The amorphous to poly-crystalline phase transition has a strong impact on the material structure, stress and subsequent growth. The kinetics of nano-scale size dependent phase transitions, such as thin film growth, are generally very difficult to study. Mo thin films, such as used in the Mo/Si system investigated here, have many applications such as short wavelength optics[1, 2] or photovoltaics[3, 4].

The Mo phase transition occurs during deposition at room temperature, making this an interesting system to study for both applications and fundamental research. The Mo phase transition can be modeled as being governed by the balance between the interfaces that stabilise the amorphous phase and the bulk Mo (Mo volume that is not part of the interface formed) that provides a driving force towards a crystalline state[5, 6], as for a bulk material this is the energetically favorable state.

The Mo/Si system is a well studied system using methods such as ellipsometry[6], ARXPS[?], *in situ* stress[7, 8, 9] and X-Ray Diffraction (XRD)[5]. The process of crystallization is difficult to study *in situ* as this involves enabling the right conditions for the transition to occur while accessible for metrology devices. For analyzing poly-crystalline structures, XRD is a very versatile method. Performing *in situ* XRD measurement has only been done very limited so far due to the need for fast measurements during growth that generally require UHV deposition chambers which are integrated into XRD beamlines at synchrotron x-ray sources[10]. *In situ* measurements on the Mo phase transition have been done by Krause et. al.[5], where the transition is modeled by assuming randomly distributed nucleation sites from which the crystallites grow in a cylindrical fashion. In the work of Krause et. al. the deposition conditions are not varied and the simulations of the model used were limited to the diffracted intensity.

In this work the sputter gas pressure of the magnetron deposition process is varied to influence the Mo growth. The sputter gas pressure affects the ad-atom energy, which is expected to affect the layer growth and phase transition[11]. The Mo growth is investigated during deposition (*in situ*) using XRR and XRD analysis. This was done at the MPI beamline of the ANKA synchrotron at the Karlsruhe Institute of Technology (KIT) as a compact laboratory source has too little intensity to perform high quality *in situ* measurements during growth.

Furthermore we analyse the Mo crystallinity by analyzing the shape of the $\langle 110 \rangle$ diffraction peak in order to separate the amorphous and poly-crystalline contributions during the transition. This is done at a reduced growth speed to enable a higher resolution, as the transition typically lasts 1 s for a 0.2 nm/s deposition speed, however the duration scales with the deposition speed, which was found in earlier experiments performed.

Figure 6.1: Schematic view of the beamline diffractometer setup. The sample is inside a UHV deposition chamber. The detector consists of both an XRD and XRR detector.

6.2 Measurement setup

The measurements described in this chapter were performed at the MPI beamline of the ANKA synchrotron. A schematic overview of the diffractometer setup is given in figure 6.1.

In order to capture part of the Mo (110) diffracted intensity during the layer growth a Pilatus 1k detector was used. The Pilatus 1k is a 2D pixel detector with 487x195 pixels and 172 μm pixel size, mounted 482 mm away from the sample center. The Pilatus captures a small but relevant part of the diffraction pattern. In particular, the Pilatus detector was mounted at a fixed detector position to measure a part of the 110 diffraction pattern *in situ* during Mo growth. To obtain more information on the structure, such as texture and strain, the Pilatus can be moved over a much larger angular range in order to perform the so-called mesh scans which are performed before and after the deposition runs. In these scans the 2D detector records a 2D image of the diffracted intensity at a grid of fixed positions along the γR and δR axis. The acquisitions at each $(\gamma R, \delta R)$ position are stitched together to form one measurement. Due to the large time needed for the extensive scan range, this cannot be done *in situ* during growth.

Two types of XRR measurements were done. The *in situ* XRR measurements were performed simultaneously with the *in situ* XRD measurements using a scintillator detector which was mounted at a fixed position with a 24 degree offset from the Pilatus in order to measure the reflected beam. The incident beam angle μ was set fixed to 2 degrees in order to have sufficient

oscillations in the signal (approximately 1 period per nm) as function of deposited thickness to model the thickness and roughness development of the layer. The XRR signal is used to estimate the rate of layer thickness increase and by modelling extract the layer roughness[5, 12, 13]. After the deposition run an XRR measurement was done where the a $\theta - 2\theta$ scan was done to determine the density of the deposited layer by analyzing the critical angle.

The X-ray energy used in the experiments was set to 12 keV by a Si crystal monochromater as this provided the highest flux and best focusing. The peak broadening due to the instrument is not more than 2 pixels on the detector in the γR direction, which corresponds to approximately 0.04 degrees.

A special deposition chamber with two large beryllium windows was used to allow *in situ* x-ray measurements. All layers were deposited onto Si(100) substrates. An amorphous 4 nm Si layer was deposited by RF magnetron deposition to have a smooth buffer layer as substrate prior to Mo deposition. This eliminates influences of the native oxide of the Si wafer. The amorphous Si buffer layer is also used for the other Mo deposition performed in this work and also matches the conditions often used in literature. The Mo was deposited on top of the amorphous Si using DC magnetron sputtering. In both cases argon was used as sputter gas. After the Mo deposition a 4 nm Si layer was deposited to cap the Mo layer in order to prevent oxidation. The magnetron to target distance was set to 125 mm. All depositions were done at room temperature using a grounded substrate holder. The Mo deposition was done at a magnetron power of 60 W. The sputter voltage was constant (within a few volts fluctuation) during layer deposition, with the exact value depending on the pressure used, with values ranging from 256 V to 315 V, for pressures ranging from 0.233 Pa to 0.547 Pa. The background pressure in the chamber was below 1e-6 mbar. The sputter gas flow rate was regulated, a Baratron pressure gauge was used to measure the pressure.

6.3 Sputter gas pressure dependence

6.3.1 Measurement results

In this section the measurements are shown and the observation done are described. The interpretation and discussion is done in section 6.3.2.

Mesh scans

In order to obtain information on the Mo texture and crystallite strain after the layer has been grown, mesh scans were performed as explained in section 6.2. A mesh scan is shown in figure 6.2. Two rings are visible, the inner ring has the highest intensity and shows three peaks in intensity along the ring.

Figure 6.2: Typical result of a detector mesh scan after stitching of separate Pilates XRD scans. Intensity is plotted as a function of γR and δR

The inner ring at $2\theta \approx 28^\circ$ is due to diffraction off the (110) Mo planes. The second ring ($2\theta \approx 40^\circ$) is the (200) peak of Mo.

χ Is defined as the angle between the diffraction vector (which bisects the angle between the incident and diffracted beam) and the sample surface normal and is more useful for plotting and interpreting the data than the γR and δR from figure 6.2. The mesh scans cover χ values from approximately -85 degrees to 85 degrees, allowing analysis of in-plane and out-of-plane lattice parameters. The mesh scan was performed before and after each deposition run consisting of Si/Mo/Si. The mesh scan before the deposition is used as background and subtracted from the measurement after deposition, which is already performed in figure 6.2. As the deposition speed varies from run to run due to the changing background pressure (from 0.075 nm/s to 0.090 nm/s), the final Mo layer thickness varied from sample to sample (typically between 12 and 15 nm, with only the 0.334 Pa deposition deviating having a 25 nm thickness). Although the mesh scans after deposition were not performed at the exact same Mo thickness for each pressure, it was observed that the measurements presented in this chapter were not strongly affected by thickness effects, i.e. the effect of varying pressure is much stronger than that of varying thickness in the thickness range observed.

The γR and δR coordinates of the mesh scan as shown in figure 6.2 are the coordinates of the measurement setup but are not suitable to analyze

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Figure 6.3: Mesh scan results for several sputter gas pressures, with the scattering vector q on the Y axis and the χ angle along the X axis

the Mo crystalline properties. In figure 6.3 the mesh scan results are transformed and plotted with the scattering vector q on the Y axis (calculated from the radial coordinates in figure 6.2) and as a function of χ on the X axis. The plot is limited to the (110) peak as the (200) peak has limited χ range. Note that due to the grazing incidence geometry of the measurement χ values below 12 degree are not accessible.

For all pressures investigated, there are clear intensity maxima visible at -60 and 60 degrees. The intensity also peaks close to the 12 degree cutoff angle in the center. For lower pressures these maxima have a higher intensity and higher contrast (peak to valley ratio along χ direction). The average q also varies along χ for lower pressures, for higher pressures it appears independent of χ , but is of lower value on average, compared to the average q value for lower pressure.

In order to evaluate the stress in the deposited layer, a $\sin^2\chi$ plot is extracted from the (χ, q) graph and shown in figure 6.4A for the lowest and highest pressure. For the lowest pressure a negative slope is visible, for the highest pressure the slope is nearly 0 but the average lattice spacing is larger ($2.80 \text{ \AA}^{-1}$ for the highest pressure and $2.82 \text{ \AA}^{-1}$ for the lowest).

The XRR measurements after deposition are shown in figure 6.4B for lowest and highest pressures. The critical angle is approximately the same for both depositions. The period of the oscillations after the critical angle differs due to the difference in layer thickness.

Figure 6.4: A) $\sin^2 \chi$ plot of the lowest pressure deposition (Blue) and the highest pressure deposition (Red), showing a difference in strain and in lattice spacing. The two curves are for the two sides of the detector capturing the same χ angle. B) *Ex situ* XRR curves for the Mo layers deposited using the lowest (red) and highest (blue) pressure

***In situ* measurements**

In order to study the dynamics of crystallization XRD measurements of the (110) peak are performed during layer deposition, with the 2D detector centered around the (110) peak at $\delta R=0$ (lowest χ value possible in this geometry). Simultaneously the *in situ* XRR measurement is performed to determine the deposition rate and model the roughness. The acquisition speed is set to 1 Hz, resulting in a typical thickness resolution of 0.08 nm, to have sufficient time resolution and detector count rate. The resulting diffraction pattern captured is summed along the χ axis to obtain a 1D diffraction curve as the χ range of the detector without a mesh scan is too small to capture useful variations along the χ axis.

The intensity of the (110) peak is plotted in figure 6.5 as a function of the deposited thickness in nm and the scattering vector q on the vertical axis. For the lowest two pressures, fringes are visible alongside the main peak. The peak width is also significantly smaller for these lower pressures.

The evolution of the peak intensity and peak width is difficult to interpret from figure 6.5. Therefore, for each thickness, the data is analyzed by fitting a Gaussian curve to the intensity. In figure 6.6A the fitted peak intensity of the diffraction peak is shown for all different pressure depositions. A step is clearly visible in the in the peak intensity, after which the peak intensity increases much faster as a function of thickness. The step in intensity is due to the amorphous to poly-crystalline phase transition, as will be explained in section 6.3.2. This transition occurs at a higher deposited thickness for increasing pressure.

In order to determine the crystallinity of the deposited layers, the integrated intensity is shown in figure 6.6B. Up to 0.448 Pa the integrated

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Figure 6.5: *In situ* XRD results for several sputter gas pressures, with the scattering vector q on the Y axis and the deposited thickness (nm) along the X axis

Figure 6.6: A) Peak intensities of the diffraction peak, determined by a Gaussian fit, B) Integrated intensity of diffraction signal

Figure 6.7: A) Peak width of the diffraction peak, determined by a Gaussian fit. The black dotted line is the peak width expected from Scherrer's equation for crystallites in size equal to the layer thickness, B) Roughness obtained from the XRR measurement for both the Si buffer and the Mo layer, for all pressures.

intensity is approximately equal and increases at the same rate. For higher pressures the integrated intensity is lower and increases at a lower rate.

The crystallinity of a layer has a strong effect on the diffracted peak intensity and peak width. For sputter gas pressures up to 0.448 Pa the peak intensity after the transition shows similar behavior with almost the same slope, as seen in figure 6.6A. The peak width drops during the transition as shown in figure 6.7A. Also the width from after the transition onwards is comparable for pressures up to 0.448 Pa. The width calculated from Scherrer's equation, when taking the deposited thickness as crystallite size, is plotted as well. Scherrer's equation is defined as:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (6.1)$$

Where τ is the average size of the crystallites. K is a dimensionless shape factor with a value close to unity which depends on the shape and structure of the crystallites. In this work $K = 0.9$ is taken, corresponding to a sphere. λ is the X-ray wavelength used, β the Full Width Half Max (FWHM) line broadening in radians and θ is the Bragg angle. Note that the crystallite size is only determined in the direction of the diffraction vector.

For 0.456 Pa and higher, the peak intensity increases at a lower rate, which further reduces with increasing pressure. Also the peak width increases with pressure (compared at equal thicknesses) for all thicknesses past the start of the transition. The integrated intensity is also lower for higher pressures. The transition width (thickness from the start to the end of the transition) also increases with increasing pressure.

In order to assess the role of roughness during growth the roughness is obtained from the *in situ* XRR measurements and shown in figure 6.7B.

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Figure 6.8: Diffracted intensity, integrated over χ , as a function of reciprocal lattice spacing, for selected thicknesses before, during and after the phase transformation, for 0.233 Pa (left) and 0.547 Pa (right)

The initial Mo growth shows a roughness increase, after which the roughness drops in the first 2 to 3 nm of Mo growth for all pressures. The continued growth then shows an increasing roughness. The roughness is also correlated to the pressure, with lower pressures having a lower roughness.

As the Mo amorphous phase and poly-crystalline phase have very distinct properties regarding peak height and intensity the diffracted intensity curve as a function of q may reveal more complex behavior than captured in single values such as peak intensity or width. To investigate this the diffracted intensity curve as a function of q is shown in figure 6.8. For 0.233 Pa the post transition crosssection (green) has a lower intensity in the tails than the pre-transition crosssection (blue), visible as a lower intensity below $2.65 \text{ \AA}^{-1}$ and above $3 \text{ \AA}^{-1}$. For 0.547 Pa the tails are still present after the transition.

6.3.2 Discussion

Mesh scans

For powder diffraction without a preferred orientation the rings visible in figure 6.2 would appear equal in intensity along the ring (assuming negligible absorption in the sample, which is valid for thin films). The fact that along the (110) diffraction ring there is a strong intensity modulation indicates there is a strong texture, i.e. a preferred orientation of the Mo crystallites developed during growth, where their (110) planes are oriented parallel to the growth surface due to their high packing density and low surface energy. The peak near the center of the ring results from the reflected beam (note that the reflected beam from the blank substrate is subtracted as background). The scan range is out of range of the direct beam.

More detail about texture and lattice spacing is obtained from the radial graphs presented in figure 6.3, which focus on the (110) diffraction signal. Although $\chi = 0$ (representing diffraction planes parallel to the sample surface) is not accessible due to the grazing incidence geometry, for low χ values the onset of a high intensity peak for the (110) diffraction signal is still visible, therefore a peak must be located at $\chi = 0$. This indicates a $\langle 110 \rangle$ texture. The additional (110) peaks observed at $\chi = -60^\circ$ and $\chi = 60^\circ$ are due to the symmetry of the (110) planes in a BCC lattice, confirming the texture is $\langle 110 \rangle$.

The contrast between peaks and valleys in radial scans is higher at the lower sputter gas pressure depositions. This can be due to a lower crystallinity at higher pressures, i.e. the presence of an amorphous phase, as amorphous Mo has no texture. This is investigated further in the next section. The widths of the peaks remains approximately similar at all pressures, indicating similar distributions of orientations (110 orientations around $\chi = 0$).

Although the out of plane $\langle 110 \rangle$ texture is apparent from the data, the in-plane (around Z) rotation of the grains is more difficult to assess. The grains have a random rotation, therefore in-plane isotropy. Due to this symmetry we can use the measurements presented in figure 6.3 to interpret the global strain. The average q of the diffracted beam at $\chi = -60^\circ, 0^\circ, 60^\circ$ reduces from around 2.84 to $2.80 \text{ \AA}^{-1}$ from lowest to highest pressure, indicating the strain is sputter gas pressure dependent. More details about strain can be obtained when the peak position is interpreted using the $\sin^2\chi$ method.

The in-plane isotropy also applies to the stress and strain. The $\sin^2\chi$ plots in figure 6.4A reveal a strong dependence of the q on χ for the lowest pressure. A near linear dependence is observed, consistent with development of biaxial stress, with some indications of an "s-shaped" trend that may occur in the presence of texture. Although it would be possible to extract a stress value from the slope of the curve, this stress only represents the stress in the crystallites, and since a significant portion of the atoms is located in grain boundaries which do not contribute to the XRD signal, the stress in the Mo crystallites does not represent the macroscopic stress of the layer. In addition, interface and surface strains modify the total stress. The negative slope shows that Mo crystallites develop under tensile stress.

In the presence of biaxial stress, a "strain free" lattice is observed when $\sin^2\chi = 2\nu/(1 + \nu)$ [14]. Using $\nu = 0.307$, this yields a "strain free" inverse lattice parameter of $q = 2.82 \text{ \AA}^{-1}$, equal to the expected literature value. For high pressure, the $\sin^2\chi$ analysis shows no significant dependence on χ , suggesting a near stress free crystallite growth, with inverse lattice parameter $q = 2.80 \text{ \AA}^{-1}$. The higher lattice distance for high pressure could be due to increased disorder, bringing the interatomic distance closer to that of the amorphous phase. Increased sputter gas incorporation may also play a role. The XRR curves were analyzed to explore the difference in density that might occur due to increased sputter gas incorporation, but no significant

difference in critical angle could be observed in figure 6.4B. Trace residues of sputter gas atoms could be further investigated using e.g. SIMS, but is beyond the scope of this chapter.

***In situ* diffraction measurements**

The *in situ* measurements presented in figure 6.5 show a strong dependence on the sputter gas pressure. At low pressures (up to 0.448 Pa) the behavior is similar: A step is observed in the intensity (figure 6.6B), associated with a transition from the amorphous to crystalline phase of the deposited material, with a resulting increase in the slope of the intensity curve after crystallization. For higher pressures (0.456 Pa and higher) it is more difficult to pinpoint the transition to crystalline growth and the slope of the intensity curve is lower and increases only gradually. These observations suggests that at higher pressures there is a reduced crystallinity during growth, possibly coupled to the presence of an amorphous phase during growth.

The fitted peak intensities and widths after crystallization for Mo layers deposited with pressures up to 0.448 Pa, shown in figures 6.6A and 6.7A, have similar values, suggesting their crystallite sizes are similar. The decreasing (peak) intensity and increasing peak width for increasing pressures above 0.448 Pa suggests that these layers have generally smaller crystallite sizes (at least in the out-of-plane direction probed here) for higher pressures, which could also be influenced by an amorphous phase being present.

The step that is observed in the peak intensity for lower pressure depositions is consistent with the process of back crystallization, where upon the phase transition from amorphous to crystalline growth, a large part of the already deposited Mo layer also transforms from the amorphous to the poly-crystalline phase. This process is thickness induced, as the Si substrate does not form a template, which plays a role in solid phase epitaxy. This results in a rapid transition from a low intensity wide peak to a high intensity narrow peak. When the peak width after crystallization is analyzed using Scherrer's equation, it appears that the crystallite size is equal to the total deposited Mo thickness. i.e. the process of back crystallization fully transforms the deposited a-Mo layer into poly-crystalline Mo.

The influence of the phase transition can also be recognized in the low intensity portion of figure 6.5, i.e. the tails of the diffraction peaks. Figure 6.8 shows cross sections of the diffraction peak at various selected thicknesses for the lowest and highest pressure. In particular, the tail of the distribution of inverse interatomic distances changes differently for low and high pressures. For low pressures the tail changes shape, it strongly reduces directly after the onset of crystallization (green curves), suggesting that the broad distribution from the amorphous phase disappeared due to backcrystallization. For high pressures there is a constantly increasing tail, showing only minor increase after the onset of crystallization is reached. This may

Figure 6.9: Transition properties, A): thickness at which the transition occurs, B): transition width (start to end) in nm.

be due to "additive" growth of a crystalline (narrow angular distribution) layer on top of the existing amorphous layer without back crystallization, or due to a smaller crystallite size resulting in more grain boundaries.

In order to further investigate the amorphous to crystalline transition that is evidenced by the step/slope change shown in figure 6.6A, linear fits are made to three separate parts of the intensity curves for each pressure: the amorphous growth region, the amorphous-to-crystalline transition region and the region where poly-crystalline growth occurs. The linear fits are indicated by dashed-dotted lines in figure 6.6A. These linear fits are used to obtain the layer thickness at the start of the transition (intersection of amorphous range fit and transition range fit) and the layer thickness at the end of the transition (intersection point between transition range fit and crystalline range fit). Figure 6.9 shows the results of the obtained thickness values for start and end of the transition, as well as the duration of the transition, as a function of deposition pressure. The actual shape of the curve is not linear but approximately an S-shaped curve. The start of the phase transition therefore occurs before the intersection of the linear curves. However, as the start of the S-curve is more difficult to determine the approximation by taking the intersection of the linear curves is used as a metric for qualitative analysis.

With increasing pressure, the thickness where the layer starts to crystallize ("crystallization thickness") initially slowly increases, with a much stronger increase of crystallization thickness occurring at pressures above 0.448 Pa. The duration of the transition similarly initially slowly increases with increasing pressure and increases rapidly after 0.448 Pa. To understand this behavior, it is instructive to correlate the changes in "moment

of crystallization" with the surface roughness. Figure 6.7B shows that for low pressure, Mo grows as a smooth layer, where the roughness before crystallization is similar or even lower than the roughness of the Si substrate layer. Above 0.448 Pa, however, the Mo roughness during growth increases much stronger. Since this transition pressure for increased roughness exactly matches the strong increase in the onset for crystallization, these two effects are very likely correlated, i.e. at pressures above 0.448 Pa the reduced particle energy and resulting low adatom mobility is no longer able to effectively smoothen layer growth, and the reduced mobility and increased morphological surface disorder also acts as a barrier for early and rapid crystallization as the rough interface stabilizes the amorphous phase.

One additional aspect of low roughnes growth is the appearance of additional intensity maxima in figure 6.5 for pressures below 0.448 Pa. Due to smooth layer growth at low pressure, and full layer (back)crystallization the crystallites in these layers have sharp boundaries (top and bottom of layer), and the diffraction signals will show typical sinc (Laue) oscillations related to a finite size effect of N lattice planes. For higher pressures (higher roughness) the crystallites can vary in size due to local variations in layer thickness (roughness) and differences in (incomplete) back crystallization which averages out the Laue oscillations for any ensemble of many crystallites.

Since the cross sections of figure 6.8 suggest that there are contributions from amorphous (broad distribution) and crystalline (narrow distribution) phases in the layer during growth, in the next section the transition is further analysed by fitting a combination of two curves to the diffraction data.

6.4 Phase transition mechanics

During the experiments carried out in this work, the phase transition of Mo from amorphous to poly-crystalline typically has a duration of 1 second. Several factor affect this duration, such as impurities[8]. In previous experiments performed (not included in this work), the transition width (in nm) was found to be invariant to the deposition speed, i.e. have a fixed width in nanometers when only the deposition speed changes. In order to investigate the Mo crystalline state during the phase transition a dedicated experiment is done where the deposition is slowed to increase the time duration of the transition.

The reduction in depositon rate is obtained by increasing the magnetron to substrate distance from 125 mm to 300mm. In combination with a 0.45 Pa sputter gas pressure and a magnetron power of 40W, this results in a decrease of the deposition speed of typically 0.08 nm/s to 0.0087 nm/s. This specific power level was chosen as the phase transition (indicated by a step in diffracted intensity) and the Laue fringes were still visible, indicating a

Figure 6.10: Illustration of the peak intensity contribution from the amorphous (red) and poly-crystalline (blue) phase, with the total diffracted intensity (green) plotted with a small positive offset

low roughness growth. Depositions using a lower magnetron power showed no Laue fringes, suggesting increased roughness, and therefore would not be representative for the results shown earlier in this chapter.

By measuring the diffracted intensity of part of the (110) diffraction peak, using the same method as described in section 6.3.2 (of which the results were shown in figure 6.6A), the transition at reduced deposition speed was determined to occur from approximately 2.9 nm to 3.3 nm. The transition width referred to hereafter refers to this interval. This interval is similar to the low pressure results described in section 6.3.2, the deviation is likely due to the different magnetron to substrate distance.

During the transition, the Mo state must be a combination of the amorphous and poly-crystalline state. In an ideal case, over the course of the transition the volume fraction of the amorphous phase reduces from 1 to 0, and the volume fraction of the poly-crystalline fraction increases from 0 to 1. Since both phases have strongly different structures, there is a measurable diffracted intensity change during the transition, as illustrated in figure 6.10. Both the peak and integrated intensity show a step during the transition, however the peak intensity shows an increased slope after the transition. Note that this is the result of the transition process averaged over the full layer.

The transition process itself is not well known. Several models can be thought of, as described in the next sections. The transition width is measurably long and not (near) instantaneous. The origin of this width may be the slow growth of the crystallites, which is referred to as a velocity limited nucleus growth model. A different origin could be that the growth

Figure 6.11: Illustration of the microscopic grain size evolution for different growth models in several snapshots in time, from top to bottom (layer cross-section view). The Mo layer on top of the substrate (black) is shown, illustrating how the amorphous phase (red) disappears and the poly-crystalline phase (blue) appears.

of a crystallite is near instantaneous but the nucleation is spread out over the transition time. This model is referred to as the flux limited growth model.

Each model corresponds to a distinct crystallite size development during the transition. As the peak width of the XRD signal is related to the crystallite size via Scherrer's equation, an *in situ* XRD measurement during the transition may determine which model is best applicable.

6.4.1 Velocity limited nucleus growth

A velocity limited growth of the crystallites is characterized by the crystallite growth starting from many nucleation sites simultaneously and expanding in size at a constant velocity until the growth is terminated by the Mo layer being fully converted to the poly-crystalline phase. The width of the transition is therefore the result of the slow crystallite growth. This process is illustrated in figure 6.11A and 6.11B.

The geometry of the velocity limited nucleus growth can be modelled in different ways, as illustrated in figure 6.11 by a cross section of the layer during the transition. An out-of-plane (top-to-bottom, figure 6.11B) growth would nucleate at the layer surface and the crystallites would grow in size downwards. The model by Krause et. al. [5] describes the crystallite growth during the transition as an in-plane growth (figure 6.11A) of cylindrical Mo crystallites.

In previous experiments, the transition width (in nm) was found to be invariant to the deposition speed (nm/s). However, a fixed crystalline growth speed (in nm/s) and a fixed nucleation density would result in a fixed transition duration (in seconds). The invariance of the transition width (in nm) to the deposition speed therefore indicates either that the crystallite

Figure 6.12: Illustration of crystallite size predicted by the different models *during* the transition.

growth velocity (in nm/s) is proportional to the deposition rate, or the nucleation site density reduces with a lowering deposition speed.

6.4.2 flux limited growth

The transition can also be described as randomly spread nucleation sites which do not initiate their growth at the same time. The crystallite growth in this model is near instantaneous compared to the deposition speed, such that no crystallites are in an intermediate size state. During the transition the number of crystallites increases, resulting in an increase in intensity during the transition.

The nucleation of a crystallite (to initiate its growth) comes from the deposition. As the layer thickness increases the crystalline phase becomes favorable and by random thickness variations or due to defects the nucleation occurs at different times, resulting in a non-instantaneous transition.

The growth of a single nucleus must also have a terminating mechanism, or crystallite growth from a single nucleation point would instantaneously crystallize the whole layer. The strain induced by the crystallization process for example may counteract the drive for crystallization and terminate the crystallite growth.

The Mo layer during the transition would consist of an amorphous phase mixed with Mo crystallites of already their final size and therefore show no size change during the transition, other than the relatively small crystallite growth due to the layer growth.

6.4.3 Distinguishing between the models

The different models presented predict different crystallite size evolution during the transition. This is illustrated in figure 6.12. Both velocity limited growth models predict a changing crystallite size during the transition. The flux limited growth model does not predict a changing crystallite size as in this model the number of crystallites increases during the transition.

Due to the geometry used we determine the crystallite size at a low χ value, which is predominantly caused by the out-of-plane crystallite size (blue in figure 6.12). Measuring at high χ values could reveal the in-plane crystallite size during growth and can be done in future experiments. In this work we focus on the out-of-plane growth properties.

If the crystallite size increases from near zero to the layer thickness over the full width of the transition, this corresponds to a velocity limited out-of-plane growth. If the crystallite size is equal to the layer thickness during the transition, the crystallite growth can either be an in-plane velocity limited growth or a flux limited growth, as the out-of-plane crystallite size during the transition is equal in both cases. To distinguish between these two options, again a measurement at a high χ value is needed in order to determine the in-plane growth properties, which is left for a future experiment.

During the transition the layer growth continues. This likely results in layer growth of the same phase as the underlying material illustrated in figure 6.11, which would result in a small positive slope added to the out-of-plane crystallite size, as illustrated in figure 6.12. As the layer thickness change (0.4 nm) over the transition is small compared to the average layer thickness during the transition (3.1nm) this is not expected to have a significant effect on the growth model.

In order to determine the crystallite size during the transition the amorphous and poly-crystalline contribution to the diffraction signal must be separated, otherwise the peak width resulting from the crystallites cannot be determined accurately. To separate the two contributions, a so called two component fit is performed, which fits a linear combination of two curves to the diffracted intensity; one for the amorphous contribution, which is expected to drop in intensity during the transition, and one for the poly-crystalline contribution, which is expected to increase during the transition. The intensity of the contributions is therefore only used to verify the separation of the two contributions.

After the fit has separated the poly-crystalline contribution from the amorphous contribution, the crystallite size of the poly-crystalline contribution can be determined from the peak width of the crystalline fraction using Scherrer's equation. The resulting crystallite size evolution is then compared to the model predictions which are illustrated in figure 6.12.

6.5 Fitting

6.5.1 Selecting fit parameters

$$f(x; A, \mu, \sigma) = \frac{A}{\sigma_g \sqrt{2\pi}} e^{[-(x-\mu)^2 / 2\sigma^2]} \quad (6.2)$$

$$f(x; A, \mu, \sigma, \alpha) = \frac{(1-\alpha)A}{\sigma_g \sqrt{2\pi}} e^{[-(x-\mu)^2 / 2\sigma_g^2]} + \frac{\alpha A}{\pi} \left[\frac{\sigma_l}{(x-\mu)^2 + \sigma_l^2} \right] \quad (6.3)$$

$$\sigma_l = \sigma_g \sqrt{2 \ln 2} \quad (6.4)$$

The experimental data is fit by either a linear combination of two Gaussian curves (shown in equation 6.2) or a linear combination of two pseudo-Voigt curves (shown in equations 6.3). The pseudo-Voigt curve is an approximation of the Voigt curve, which is a convolution of a Gaussian and Lorentzian curve. The approximation is done by taking a linear combination of a Gaussian and Lorentzian curve. The combination is determined by the mixing factor that defines the ratio between the Gaussian and Lorentzian contribution.

The amplitude of the diffraction peak is given by A and the position of the peak by μ . The peak width of the curve is given by σ_g and σ_l for the Gaussian and the Lorentzian peaks, respectively, with equation 6.4 defining the ratio between the two in order to have a matching FWHM. α is the mixing parameter of the pseudo-Voigt curve. For the double pseudo-Voigt curve the mixing parameter is kept fixed as leaving this free would introduce extra degrees of freedom which can lead to higher fit uncertainties. The resulting curve is a function of the diffraction angle x .

The starting parameters of the two component fit were selected from a single component fit by taking the single component fit parameters from before the transition as the starting parameters for the amorphous contribution, and the single component fit parameters from after the transition as the starting parameters for the crystalline contribution. For the pseudo-Voigt the mixing parameters were also selected from before and after the transition and were kept fixed during the two component fit.

It was found that, because the fit of two components to amorphous contribution was overdimensioned (too many degrees of freedom), it had the tendency to fit the wide peak using two narrower curves. Therefore the position of the curve, with the fit starting values matching the amorphous phase, was kept fixed. This removes one degree of freedom, resulting in 5 degrees of freedom for the two component fit in total (both for the Gaussians as well as the pseudo-Voigt fit). This had no significant impact on the peak width fit results during the transition but improved the separation of the two contributions outside the transition.

6.5.2 Fit results

As described in subsection 6.4.3, at the start of the transition there should (ideally) only be an amorphous contribution and at the end only a polycrystalline. For a (near) complete back crystallization (for example as seen in figure 6.7A for 0.233 Pa) the out-of-plane crystallite size is equal to the layer thickness, indicating a complete back-crystallization. A complete back crystallization was directly observed by Fillon et. al. [8]. For a perfect separation of the two components, the fit result must reflect this by having

Figure 6.13: The experimental data at 3 nm deposited (halfway the transition), showing the 2 component fits and a 1 component fit

the appropriate contribution near zero in intensity before and after the transition. The intensity can therefore be used to check the separation of the fit of the two contributions.

A single component fit curve would fit the amorphous contribution at the start of the transition and fit the poly-crystalline contribution at the end of the transition. During the transition however, it would attempt to fit 2 contributions with one curve, which would result in high inaccuracies as demonstrated in figure 6.13, where the x-ray diffraction signal near the halfway point of the transition (3 nm deposited) is plotted together with the fit results. The green curve is therefore only given as reference for the asymptotical behavior for the two component fit, before and after the transition. The large difference in fit accuracy during the transition between a one component and two component fit already justifies the use of a two component fit.

Gaussian fit

Figure 6.14 shows the result from a double Gaussian curve fit to the experimental data, with red and blue curves indicating the fit parameters for each component. The reference fit result from a single Gaussian curve is included in green. The thickness range shown is 2 to 4 nm, focused around the phase transition that is indicated by the vertical dashed lines. For layer growth before and after the transition, there is no match between the reference single component fit and the two component fit, indicating that the double Gaussian fit does not separate the two contributions accurately when one contribution dominates. During the transition both the contributions are not close to zero anymore and therefore can be separated better (as

Figure 6.14: Result of the double Gaussian curve fit, A) Intensity of the signal, B) peak width of the curve

demonstrated in figure 6.13), therefore the fit during the transition is still analyzed.

The intensity of the poly-crystalline contribution (plotted in blue) increases during the transition and the intensity of the amorphous contribution (plotted in red) drops, as seen in figure 6.14. During the amorphous phase (< 2.8 nm) there are oscillations visible in the intensity. Both contributions are in (anti) phase and also in (anti)phase with the oscillations in peak width as plotted in figure 6.14B. This is due to the fit being overdimensioned. The amorphous contribution is not properly Gaussian and the fit oscillates between fitting the broad distribution with one broad gaussian, or two narrower Gaussians of lower intensity with different peak positions.

The peak width of the double Gaussian curves is given in figure 6.14B and shows the peak width of the polycrystalline contribution is close to the peak width calculated for crystallites equal to the layer thickness in size using Scherrer's equation, for the complete width of the transition, suggesting crystallite sizes similar in size as the layer thickness throughout the transition.

Pseudo-Voigt fit

Figure 6.15 shows the result from a double pseudo-Voigt curve in red and blue for each pseudo-Voigt fitted. The reference fit result from a single

Figure 6.15: Result of the double pseudo-Voigt curve fit, A) Intensity of the signal, B) width of the curve

pseudo-Voigt curve is included in green. The transition interval is indicated by vertical dashed lines. For layer growth after the transition, there is a good overlap between single and double Voigt peak fits, indicating that, unlike the case for a double Gaussian, a double Voigt is able to fit the data, even when one component dominates.

The intensity in figure 6.15A shows the amorphous contribution reducing steeply during the transition and the poly-crystalline contribution increasing, as expected. The amorphous phase however does not reduce fully to zero, this can be due to fit inaccuracies or possibly due to grain boundaries that are still present. The poly-crystalline contribution may then consist of a crystallite and a grain boundary contribution.

The peak width of the fit is plotted in figure 6.15B. The black curve included is calculated from Scherrer's equation by using the deposited layer thickness as crystallite size. For a fully transitioned layer (a complete back crystallization) the experimentally obtained peak width should be near the calculated value after the transition. The peak width of the fit corresponding to the poly-crystalline contribution (blue curve) is not accurate up to 2.9 nm due to the low intensity of the poly-crystalline contribution. This results in a peak width that is smaller than the peak width obtained from Scherrer's equation, which would indicate crystallites that are far larger than the layer thickness which is not possible. Due to the low roughness the Mo thickness even locally does not exceed the layer thickness significantly,

Figure 6.16: Crystallite size as determined via Scherrer's equation plotted as a function of deposited Mo thickness. The interval of the transition from amorphous to poly-crystalline is indicated by vertical dashed lines

therefore there is no Mo present to make a crystallite with an out-of-plane size significantly larger than the Mo layer thickness. Therefore the peak width is only considered to be accurate at >2.9 nm Mo deposited.

During the transition the peak width of the poly-crystalline contribution is close to the black curve, indicating a crystallite size close to the layer thickness. The peak width of the amorphous contribution, shown by the red curve in figure 6.15B, increases strongly during the transition. This increase is significant since the peak intensity is still high enough to obtain a good quality fit. The peak width of the amorphous contribution halfway the transition (point of equal intensities at 3 nm) corresponds to a coherence length or "crystallite size", of over 1 nm. This suggests a "quasi-crystalline" state or a more well-defined nearest or nearest-nearest neighbour interatomic distance. As the crystallites form, these quasi-crystalline domains disappear and only highly amorphous material (i.e. a large spread of interatomic distances), such as grain boundaries, are left.

Comparing fit results

For both the double Gaussian (figure 6.14) and the double pseudo-voigt (figure 6.15) fits the poly-crystalline contribution (blue curves) has a diffraction peak width during the transition that is close to the peak width that is ex-

pected for a fully crystallized layer. A more convenient representation of these graphs is given in figure 6.16, where the crystallite size as determined through Scherrer's equation is compared with the deposited thickness. The crystallite size during the transition shows similar behavior for both the Gaussian and the pseudo-Voigt fits. It is therefore likely that the bad separation of the gaussian fit of the two contributions at the start and end of the transition did not affect the peak width of the fit result during the transition.

Discussion

For both types of fits, the crystallite size at the start of the transition (left dashed line) is approximately 2.2 nm, which slowly increases to about 3 nm at the end of the transition. This is near the deposited layer thickness for the full duration of the transition and therefore there is no significant out-of-plane crystallite growth observed. This matches with the prediction for a flux limited growth or an in-plane velocity limited growth, as seen in figure 6.12. The out-of-plane velocity limited growth model can now be rejected due to the 2.2 nm crystallite size already present at the start of the transition.

Both fits show that after the transition, there is a small but constant (0.25 nm) difference between the crystallite size and the layer thickness. Since uncertainties in data analysis (error in thickness calibration, strong instrumental broadening, integration or fitting artifacts) would generally be different for different thicknesses (e.g. narrow peaks would be affected more strongly by instrumental broadening than broad peaks), the origin of this offset is believed to be of a physical nature. The interface formation may account for the offset, as the first 0.25 nm of Mo deposited may form an amorphous silicide which does not take part in the Mo phase transition and does not contribute to the crystallite size.

Figure 6.16 shows that, after the near instantaneous crystallization to a crystallite size of 2.2 nm, during the transition there is an increase in crystallite size that is more rapid than explained by the layer growth alone, which is not predicted by the models initially presented. It should be noted that these models represent simplified cases that may not fully represent the real crystal shape and growth. In addition, the crystallite size is determined in a direction that is 12 degree off the surface normal, where an in-plane component of crystal growth could effectively lead to the observed increase of the crystallite size. However, the main conclusion remains that near instantaneous crystallization of a large out-of-plane crystallite size is observed, which suggests either flux limited or in-plane velocity limited crystal growth.

To distinguish between the flux limited growth model and the velocity limited growth model the experiment and analysis should be repeated at a high χ value to determine the in-plane growth. An increasing in-plane

crystallite size during the transition would suggest an in-plane velocity limited growth model, a constant crystallite size would suggest a flux limited growth mode. Repeating the experiment for a range of χ values also would allow extrapolation to $\chi = 0$.

6.6 Conclusions

The effect of sputter gas pressure on growth of Mo onto a-Si was studied using *in situ* XRD, where sputter gas pressure was varied from 0.233 Pa to 0.547 Pa. The Mo shows polycrystalline growth, with a strong (110) texture at all pressures. The depositions at the lower side of this range have crystallites with an in-plane compressive growth stress, and a much larger crystalline volume for the same deposited thickness, compared to depositions done at the higher side of this pressure range. The *in situ* measurements of the (110) diffraction peak show the phase transition is delayed (at a higher deposited thickness) and has an increased duration for increasing pressure. The roughness also increases with pressure, for the lower pressures the roughness was significantly lower and Laue oscillations were visible. The back crystallization (i.e. the phase transition of the already deposited material) is likely partial or absent for higher pressures, leading to a reduced crystalline volume. These changes in the Mo growth properties are likely due to the reducing ad-atoms energy with increasing pressure.

In order to investigate the kinetics of the phase transition a separate experiment was performed at a reduced deposition speed in order to increase the transition duration in time, allowing more precise *in situ* measurements during the transition. During the transition both an amorphous phase and a poly-crystalline phase are present. These two contributions were fitted using a two component fit in order to analyze the poly-crystalline contribution separately. The width of the diffraction peak of the poly-crystalline contribution was analyzed using Scherrer's equation and indicated an out-of-plane crystallite size that appeared to grow very fast, near-instantaneously reaching a value of 2.2 nm at the start of the transition. Both an in-plane velocity limited growth model and a flux limited growth model are consistent with the results, and further distinguishing between them will require *in situ* XRD measurements during growth where diffracting planes with a large offset angle to the surface are investigated. The results shown here do not support an out-of-plane velocity limited growth model which is characterized by a crystallite size starting at zero size at the start of the transition.

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Summary

The research described in this thesis has been aimed to improve the understanding of thin film growth by analysing the growth stress in highest, i.e. atomic level detail. This is done by in-situ stress measurement of the growth of, primarily, nanoscale Mo/Si layer systems and relating the data to in-situ X-Ray Diffraction (XRD) and ex-situ Low-Energy Ion Scattering (LEIS) measurements. Physical processes, such as compound formation, phase transitions and diffusion could thus be observed. The stresses that originate from these effects typically act at length scales from the inter-atomic distance to several nanometer (typically corresponding to the layer thickness or lateral grain size in the films). As these effects occur uniformly over the full surface of the thin film (provided the substrate and deposition process are homogeneous), a macroscopic force develops which acts on the substrate, inducing a measurable curvature in thin substrates.

So far, measuring growth stresses accurately during deposition has been challenging due to the ultrahigh vacuum conditions required as well as the presence of electrical interference from the plasma of the sputter process. For this reason, a setup was developed that continuously measures the curvature of a cantilever during layer growth, from which the intrinsic stress of the deposited layer was calculated. The measurement is done optically to avoid electrical interference. A self-contained, in-vacuum, in-situ thin film stress measurement tool was developed. This tool records the intrinsic stress with a low noise level of 0.01 N/m RMS, sufficiently sensitive to capture features such as the transition of Mo from an amorphous to a poly-crystalline phase. The measurement range was over 600 N/m and likely limited by the mechanical limit of the cantilever curvature or non-linearities in the stress-curvature relation (Stoney equation). The tool was controlled wirelessly when inside the deposition setup with a live view of the stress evolution during deposition.

In order to better understand the development of growth stresses in Mo/Si systems, the stress measurements were correlated with LEIS measurements. The combined analysis allowed an accurate understanding of the interface formation occurring and its effect on the stress development. A tensile peak in the first 0.15 nm was observed, corresponding to a (fast saturating) process suggested to be related to grain boundary filling. After this initial tensile growth stage, a compressive growth was observed. This compressive stress was related to silicide interface formation, a process reducing with the amount of Mo available at the surface, as evidenced by

LEIS data. Furthermore, the LEIS data during this growth stage showed a surface density that was much higher than a mixed coverage of Mo and Si, with further evidence of interface compound formation playing an important role in the development of stress. At 1.5 nm layer thickness, the bulk Si growth started, shown by LEIS as the closing of the Si layer and by a constant stress of 1.1 GPa, mainly due to peening from energetic Si atoms.

The Mo-on-Si stress development showed a strong tensile stress due to interface formation, likely due to defects created in the Si surface upon MoSi₂ formation. The LEIS measurements indicated a larger intermixing, shown by surface atomic densities of Mo and Si being higher than expected from a mixed coverage of Mo and Si and resulting in an interface width more than twice as large as in the case of Si-on-Mo. The phase transition of Mo was clearly observable in the stress development by a tensile step of 0.7 N/m at 2.1 nm of Mo deposited.

The Mo-on-Si interface was modified by using C and Ru interlayers in order to understand the effect of substrate layers (in particular the effect of diffusion of substrate atoms into Mo) on the stress development of Mo growth. Even a 0.1 nm C layer, equivalent to less than a monolayer, had a strong impact on the Mo stress development, likely due to the high diffusivity of C in Mo. Ru on the other hand had a low diffusivity in Mo and, similar to Mo, formed a silicide with the a-Si substrate layer. Due to the similar physical properties of Ru and Mo, the Ru interlayer acted as a template for the Mo layer. This was concluded from the fact that the Mo-on-Ru-on-aSi stress development was equal to the Mo stress development at a later stage, corresponding to a continued growth of Mo-on-Mo. Due to this templating effect, the Mo phase transition occurred earlier, whereas for the C interlayer it was postponed due to C diffusing into the Mo. Both C and Ru reduced the Mo/Si intermixing and reduced the initial tensile stress of the Mo growth associated with the silicide formation.

It has long been recognized that the film structure and stress development of Mo do not only depend on the substrate layer it is deposited on, but also on the growth conditions, and in particular on the deposition pressure. The dependence of the crystalline structure of Mo on the pressure during deposition was studied using in-situ XRD. With increasing sputter gas pressure the amorphous to poly-crystalline phase transition was delayed and the back crystallization became only partial or absent. For the low pressure deposition the roughness was the lowest and Laue fringes were visible after the phase transition.

The phase transition of Mo was analyzed in more detail by performing a 2 component fit. In this approach the diffraction peak is fitted by a linear combination of either two Gaussian or two pseudo-Voigt curves to separate the amorphous and poly-crystalline contributions during the transition. The width of the diffraction peak corresponding to the poly-crystalline contribution was analysed using Scherrer's equation. It indicated an out-of-plane crystallite size nearly equal to the deposited thickness during the complete

transition, indicating that the crystallite growth is in-plane. These measurement can further lead to a better understanding of the Mo phase transition kinetics.

Samenvatting

Het onderzoek beschreven in deze thesis is er op gericht om het begrip van dunnelaaggroei te verbeteren doormiddel van het analyseren van de groei stress in het hoogste, dat is atomair, detail. Dit is gedaan door in-situ stress metingen van de groei van hoofdzakelijk Mo/Si gelaagde systemen en door deze data te relateren aan in-situ röntgen-diffractie (XRD) en ex-situ Lage-energie ionen verstrooiing (LEIS) metingen. Fysische processen, zoals het vormen van chemische verbindingen, fase-overgangen en diffusie konden hierdoor geobserveerd worden. De stress veroorzaakt door deze effecten speelt typisch op lengteschalen van de inter-atomaire afstand tot enkele nanometers (typisch overeenkomend met de laagdikte of kristallietgrootte in de laag). Aangezien deze effecten homogeen over het gehele oppervlak van de dunne laag plaatsvinden (aangenomen dat de dunne laag homogeen is aangebracht), zal er een macroscopische kracht ontstaan die op het substraat werkt, wat een buiging teweegbrengt.

Het nauwkeurig meten van de groei stress is uitdagend door de ultrahoge vacuümomgeving die nodig is en ook door de aanwezigheid van elektrische interferentie die afkomstig is van het plasma van het depositie proces. Daarom is er een opstelling ontwikkeld die de buiging van een cantilever continue meet tijdens de laaggroei. Deze buiging kan worden omgerekend naar de intrinsieke stress van de gedeponeerde laag. De meting is optisch gedaan om de elektrische interferentie te vermijden. Een op zichzelf staande, vacuüm geschikte in-situ stress meetinstrument is ontwikkeld. Dit instrument meet de intrinsieke stress met een ruisniveau van 0.01 N/m RMS, wat voldoende gevoelig is om laaggroei kenmerken zoals de fase-overgang van Mo van amorf naar poly-kristallijn te meten. Het meetbereik was meer dan 600 N/m en is waarschijnlijk beperkt door de mechanische limiet van de buiging van de cantilever of door niet-lineariteiten in de stress-buiging relatie (Stoney's vergelijking). Het instrument was draadloos bedienbaar wanneer deze zich in de depositie-opstelling bevond met een directe uitlezing van de stressontwikkeling tijdens de laaggroei.

Om de groeistress in Mo/Si systemen beter te begrijpen zijn de stress metingen vergeleken met LEIS metingen. De gecombineerde analyse bracht een beter begrip van de grenslaag vorming die plaatsvindt en het effect hiervan op de stress ontwikkeling. Een trekspanningspiek in de eerste 0.15 nm was waargenomen, overeenkomend met een snel verzadigend proces wat mogelijk gerelateerd is aan het vullen van korrelgrenzen. Na deze initiële piek was een groei met een drukspanning waargenomen. Deze is gerelateerd aan

de silicide vorming aan de grenslaag, een proces dat afneemt met de hoeveelheid Mo die beschikbaar is aan het oppervlak, aangetoond door de LEIS metingen. Daarnaast lieten de LEIS metingen een atomaire oppervlaktedichtheid zien die hoger was dan een samengesteld Mo en Si oppervlak. De vorming van verbindingen aan de grenslagen blijkt een belangrijke rol te vervullen in de stressontwikkeling. Bij 1.5 nm laagdikte begint de bulkgroei van Si, wat zichtbaar is in de LEIS metingen als het sluiten van de laag en in de constante stress van 1.1 GPa, hoofdzakelijk door het neerslaan van energetische Si atomen.

De Mo-op-Si stress ontwikkeling liet een sterke trekspanning zien door de grenslaag vorming, waarschijnlijk door defecten die in het Si oppervlak gecreëerd worden bij MoSi_2 vorming. De LEIS metingen laten een grotere vermenging van de lagen zien, zichtbaar door een hogere atomaire oppervlaktedichtheid van Mo en Si dan verwacht op basis van een gedeelde Mo en Si dekking. De grenslaag die gevormd wordt is meer dan twee keer zo groot dan in het geval van Si-op-Mo. De faseovergang van Mo was duidelijk zichtbaar in de stress ontwikkeling door een trekspanningspiek van 0.7 N/m bij een gedeponeerde Mo dikte van 2.1 nm.

De Mo-op-Si grenslaag was gewijzigd door C en Ru tussenlagen om zo het effect van de onderlaag (in bijzonder het effect van diffusie van onderlaag atomen in Mo) op de stressontwikkeling van de Mo groei te bepalen. Zelfs een 0.1 nm C laag, equivalent aan minder dan een enkele atoomlaag, had een sterke invloed op de Mo stress ontwikkeling, waarschijnlijk door de hoge diffusiviteit van C in Mo. Ru daarentegen had een lage diffusiviteit in Mo en vormt, net als Mo, een silicideverbinding met de α -Si onderlaag. Door de vergelijkbare eigenschappen van Ru en Mo diende de Ru laag als een sjabloon voor de Mo groei. Dit is geconcludeerd uit de grote overeenkomst tussen de Mo-op-Ru stress ontwikkeling en de Mo-op-Si stress ontwikkeling in een later stadium van Mo groei, overeenkomend met een voortzetting van Mo-op-Mo groei. Door dit sjablooneffect vond de Mo faseovergang eerder plaats, waar de C tussenlaag de faseovergang juist vertraagde door de C diffusie in het Mo. Zowel C and Ru verminderde de Mo/Si vermenging en verminderde de initiële trekspanning van de Mo laag die afkomstig is van de vorming van silicide verbindingen.

Het is bekend dat de structuur en de stressontwikkeling van dunne Mo lagen niet alleen afhangt van de onderlaag, maar ook van de groeicondities, en in het bijzonder van de gasdruk tijdens het deponeren van de laag. De invloed van de gasdruk tijdens de depositie op de kristallijne structuur van het Mo was bestudeerd door in-situ Röntgendiffractie (XRD) te gebruiken. Met een toenemende gasdruk vertraagde de amorf naar polykristallijn faseovergang en nam de omzetting van het al gedeponeerde materiaal naar de polykristallijne fase af of verdween zelfs volledig. De ruwheid was het laagst voor de lage gasdruk depositie, mede hierdoor waren Laue oscillaties goed zichtbaar in de XRD data na de faseovergang.

De faseovergang is in detail bestudeerd door de diffractiepieken met een

twee-componentenfunctie te analyseren. In deze aanpak wordt de diffractiepiek benaderd door een combinatie van Gaussische of pseudo-Voigt functies. Deze aanpak is zeer geschikt om de amorfe en polykristallijne contributies tijdens de faseovergang te scheiden. De breedte van de diffractiepiek overeenkomend met de polykristallijne contributie is geanalyseerd met behulp van de vergelijking van Scherrer. Hieruit bleek een kristallietgrootte die bijna gelijk was aan de laagdikte in de richting loodrecht op het oppervlak voor de gehele duur van de faseovergang. Hieruit blijkt dat de kristallietgroei voornamelijk in het vlak van het oppervlak plaatsvindt. Deze metingen kunnen leiden tot een beter begrip van de mechanismes van de faseovergang.

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