Department of Physics, Chemistry and Biology

Master's Thesis

Off-normal Film Growth by High Power Impulse Magnetron Sputtering

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In this study we contribute towards establishing the process-microstructure relationships in thin films grown off-normally by ionized physical vapor deposition. High power impulse magnetron sputtering (HiPIMS) is used at various peak target powers and deposition rates to grow copper (Cu) and chromium (Cr) films from a cathode placed at an angle 90 degrees with respect to the substrate normal. Films are also deposited by direct current magnetron sputtering (DCMS), for reference. Scanning electron microscopy is employed to investigate column tilting and deposition rate while X-ray diffraction techniques are utilized to study crystal structure and grain tilting.

It is demonstrated that the columnar structure of Cu tilts less with respect to the substrate normal as the peak target power increases, which has been shown to correspond to a higher ionization degree of the sputtered material [1]. One explanation for this is that the trajectories of the ions are deflected towards the substrate and therefore deposited closer to the normal, as has been suggested in the literature (see e.g. [2]). Energetic bombardment by ions might also increase surface mobility, which further raises the columns. It is also concluded that the change in tilting is not caused by a lower deposition rate obtained when employing HiPIMS. The same is not seen for Cr, where all deposited films exhibit the same tilting angle. When the column tilting of Cu and Cr is compared a large difference is observed, where the columns of Cr are closer to the substrate normal. The reasons for this difference are discussed in light of nucleation and growth characteristics in the two materials.

X-ray diffraction analysis reveals that Cu films exhibit an (111) fiber texture. Comparison of films grown by DCMS and HiPIMS shows that in the HiPIMS cases the grains are closer to the surface normal and better oriented with each other. In the case of Cr both DCMS and HiPIMS grown films are (110) biaxially aligned.

HiPIMS, HPPMS, glancing angle deposition
Kunskapens rot är bitter, men dess frukter är söta.
- Cicero
Abstract

In this study we contribute towards establishing the process-microstructure relationships in thin films grown off-normally by ionized physical vapor deposition. High power impulse magnetron sputtering (HiPIMS) is used at various peak target powers and deposition rates to grow copper (Cu) and chromium (Cr) films from a cathode placed at an angle 90 degrees with respect to the substrate normal. Films are also deposited by direct current magnetron sputtering (DCMS), for reference. Scanning electron microscopy is employed to investigate column tilting and deposition rate while X-ray diffraction techniques are utilized to study crystal structure and grain tilting.

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Chapter 1

Introduction

1.1 Motivation and state-of-the-art

Thin films grown by physical vapor deposition (PVD) techniques often exhibit a columnar microstructure \[3\], which originates when atoms from the vapor phase condensate on a surface (substrate) forming stable atomic islands (nuclei). As more atoms arrive the islands grow in size and coalesce forming columns. When the vapor incidents from normal or near normal direction with respect to the substrate surface straight columns are obtained with different size and shape depending on the material being used as well as on the process parameters \[4,5\]. Off-normal deposition is commonly the case when coating trenches or three-dimensional objects. It is also explicitly employed to grow films and when the angle of incidence is very shallow (larger than 80° with respect to the surface normal) the deposition method is referred to as glancing angle deposition (GLAD). GLAD is used to fabricate films, which find application as e.g. anti-reflective coatings \[6\] or three-dimensional photonic crystals \[7\].

Deposition at glancing angles results in shadowed regions behind the initially formed nuclei \[3,8,9\]. No additional atoms are therefore supplied from the vapor to the shadowed areas, preventing coalescence of islands. Since deposition only is done on the non-shadowed part of the islands, separated columns grow towards the direction of the incident vapor. The angle of tilting from the surface normal is though always smaller than the incident angle of the vapor.

The shadowing effect can be detrimental for the film quality, especially when dense coatings of three-dimensional objects are desired. GLAD instead relies on
the shadowing effect to create nanostructured films where the columnar structure can be engineered into e.g. helicals, vertical posts and zig-zag patterns or as a combination thereof. To obtain control of tilting angle, separation and uniformity of columns are therefore crucial when depositing GLAD structured films or dense coatings on three-dimensional objects to yield desired properties.

Changing the incidence angle of the incoming vapor can modify the degree of tilting of the columnar structure, but there are also other ways to affect it. Surface diffusion is counteracting the effect of shadowing by moving adatoms from regions with high concentration towards areas with lower concentration. This means that adatoms move from the tip of the column towards the shadowed region. Thus, by raising the substrate temperature the adatom mobility increases and causes the columns to tilt less with respect to the substrate normal. On the one hand, increase of the deposition rate counteracts the effect of diffusion since adatoms are capped more rapidly decreasing the diffusion length and therefore yielding larger tilting of the columns. Another way to control the column tilting is by changing the deposition pressure. Increase of the deposition pressure leads to a more pronounced gas phase scattering, which in turn results in a broader distribution of the incident vapor causing the columns to stand closer to the substrate normal.

A large portion of ions in the incident vapor can also facilitate control over the column tilting. As the ions approach a grounded substrate their trajectories can be deflected towards the surface normal due to the potential difference between the plasma and the ground. This effect can be more pronounced when the substrate is electrical isolated (floating) or even when a substrate bias potential is applied. High power impulse magnetron sputtering (HiPIMS) is a PVD technique that can generate ultra dense plasmas that yield a higher ionization degree of the sputtered material as compared to other sputtering based techniques, e.g. direct current magnetron sputtering (DCMS). The larger ion fluxes available in HiPIMS have been reported to enable filling of μm size trenches by copper as well as off-normal deposition of uniform tantalum films. The same has been shown to be the case when depositing TiAlN coatings on cutting inserts. Furthermore, HiPIMS has been demonstrated to enable growth of films that exhibit columns closer to the substrate normal as compared to DCMS when chromium and tantalum are deposited at ninety degrees off-normally. It has also been shown that the columns are raised towards the normal as the amount of chromium ions increase when a large bias voltage is applied.
1.2 Objectives and research strategy

The fundamental mechanisms that determine the off-normal growth are not well understood. It is believed that ions can be deflected towards the substrate surface and raise the columnar structure, but it is not known to which extent this occurs. Energetic bombardment by ions can also have a substantial impact since this may affect both surface diffusion and nucleation density, which also may have implications on the column tilting.

This work is carried out in order to contribute towards the understanding of the off-normal growth process through numerous depositions. Two different materials, copper and chromium, are employed in the deposition procedure. The characteristic difference between them is the adatom mobility, where copper is a high and chromium a low mobility material. They are used to grow films on grounded substrates, which are employed in order to investigate if the introduced potential difference between the plasma and the substrate is enough to affect the ions in such a way that the column tilting is modified. Both HiPIMS and DCMS deposition processes are utilized in order to study the effect of a larger portion of ions in the incident vapor, where the former is used at different pulsing frequencies to achieve different degrees of ionization and the latter as reference with a low ionization degree.

The cross-sectional views of all films are analyzed in a scanning electron microscope (SEM) where the column tilting angle is measured together with the film thickness. In addition, the films with the lowest (DCMS) and highest (HiPIMS) degree of ionization for each material are investigated with X-ray diffraction (XRD) techniques to examine how the crystal planes are influenced by the larger amount of ions.

1.3 Outline

The outline of the chapters following the introduction is presented below. First the theory of deposition, especially sputtering, is reviewed together with the growth of thin films (chapter 2). In chapter 3 it is described how the films are grown in this study. This chapter does also describe the experimental techniques that are used. Chapter 4 contains and discusses the obtained results. The results are then summarized in chapter 5. Finally an outlook of the future is given (chapter 6), which hopefully can give some inspiration to further work.
1.4 Definitions

1.4.1 Variables and constants

<table>
<thead>
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<th>Symbol</th>
<th>Quantity</th>
<th>SI unit</th>
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<tr>
<td>B</td>
<td>magnetic field</td>
<td>$T = V s/m^2$</td>
</tr>
<tr>
<td>$\mathbf{d}_{h,k,l}$</td>
<td>interplanar spacing</td>
<td>m</td>
</tr>
<tr>
<td>E</td>
<td>electric field</td>
<td>V/m</td>
</tr>
<tr>
<td>F</td>
<td>force</td>
<td>$N = kgm/s^2$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>surface free energy</td>
<td>$J/m^2 = kg/s^2$</td>
</tr>
<tr>
<td>f</td>
<td>frequency</td>
<td>Hz $= s^{-1}$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
<td>m</td>
</tr>
<tr>
<td>n</td>
<td>plasma density</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$n_e$</td>
<td>electron density</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$n_i$</td>
<td>ion density</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>q</td>
<td>electric charge</td>
<td>C $= As$</td>
</tr>
<tr>
<td>S</td>
<td>sputtering yield</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\theta$</td>
<td>angle</td>
<td></td>
</tr>
<tr>
<td>v</td>
<td>velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$V_f$</td>
<td>floating potential</td>
<td>V</td>
</tr>
<tr>
<td>$V_p$</td>
<td>plasma potential</td>
<td>V</td>
</tr>
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1.4.2 Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Explanation</th>
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<tbody>
<tr>
<td>CADR</td>
<td>constant average deposition rate</td>
</tr>
<tr>
<td>CAP</td>
<td>constant average power</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>DCMS</td>
<td>direct current magnetron sputtering</td>
</tr>
<tr>
<td>DP</td>
<td>different powers</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>GLAD</td>
<td>glancing angle deposition</td>
</tr>
<tr>
<td>HiPIMS</td>
<td>high power impulse magnetron sputtering</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>QCM</td>
<td>quartz crystal microbalance</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
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</table>
Chapter 2

Thin Film Deposition and Growth

2.1 Overview

There are a number of different techniques for deposition of thin films available today. In general they can be divided into two different categories, chemical vapor deposition (CVD) and physical vapor deposition (PVD). The former uses volatile gases to transport the source materials. When the gases arrive at the deposition chamber chemical reactions are triggered if the temperature is high enough resulting in a coating on all surfaces inside the chamber. Some by-products, in the form of gases, are also created and are transported away from the deposition chamber. The high temperatures utilized in CVD are though not always applicable when producing thin films. It can, for example give rise to recrystallization of the film and/or melting of the substrate.

The latter of the two, PVD, uses solid source materials, which are transformed into vapor by physical means before condensing on a surface. The transformation can be accomplished by utilizing thermal, electric or kinetic energy. Thermal energy is used in thermal evaporation where the source material is heated until it evaporates. The electric energy is employed in arc evaporation where a high current is used to melt a small spot of the source material. Sputtering is the name of the technique that utilizes the kinetic energy through transfer of momentum and energy. Its concept is further explained in the upcoming sections.
2.2 Sputtering

Sputtering is a process where atoms from a solid source material, referred to as target, are ejected into gas phase by physical means. This is accomplished by letting high energetic particles, normally ions, bombard the target. As the ions impinge on the surface of the target, collisions take place, which in turn cause transfer of momentum and energy. If energy and momentum are transferred to atoms in the surface layers they can be ejected from the surface, i.e. be sputtered.

There are a lot of possible interactions that can take place when an ion strikes the surface. It can stick to the surface, be implanted or reflected back. Bombarding ions can lead to displacement or sputtering of atoms in the surface region. They can also cause secondary electrons\(^1\) and photons. A cascade of different types of interactions are also possible. The types of interactions that take place are strongly dependent on the type of ions and their energy as well as the choice of target material. The ions used for sputtering are normally argon, but other heavier inert gases are also applicable. In order to sustain the sputtering process in thin film deposition a plasma is used, explained in section 2.2.1.

An important parameter in the sputtering process is the number of sputtered atoms per incoming ion. This parameter is known as the sputtering yield, \(S\), and depends also on the choice of target material and inert gas as well as the energy of the bombarding ions. Values ranging from \(10^{-1}\) to 10 are typical for the sputtering yield \([21]\).

2.2.1 Plasma

Plasma is a term that describes a partially ionized gas. It is known as the fourth state of matter since its properties are different from ordinary gases, liquids and solids. It is further believed to make up 99 % of the visible universe \([22]\).

A plasma is quasineutral, meaning that the electron density, \(n_e\), and the ion density, \(n_i\), are the same when averaged over a large volume. The quasineutrality of the plasma is though not valid everywhere if the plasma is confined inside a vacuum chamber. It is broken where the plasma gets in contact with a conducting surface, e.g. the walls of the chamber. So-called sheaths build up close to the walls, where the number of ions are much larger than the number of electrons,

\[1\] Secondary electrons are electrons that are generated or knocked out from an atom in an inelastic collision between the impinging ions and the atoms of the target.
2.2 Sputtering

\( n_i > n_e \). This is caused by the difference in velocity of the electrons and ions. The electrons move much faster than the ions. Therefore, they leave the plasma more often and are lost to the chamber walls resulting in a positive net charge density in the sheaths. By accounting for this criterion when solving Poisson’s equation it is shown that the plasma potential, \( V_p \), is positive relative to the walls \(^{[23]}\). The walls of the chamber are often grounded, yielding a positive plasma potential of a couple of volts. An illustration of the potential between two plates, a negative cathode and a grounded anode, with plasma in between is illustrated in figure 2.1.

\[
\begin{array}{c}
V_p \\
0 \\
-\mathbf{V} \\
\end{array}
\]

Figure 2.1: Schematic representation of the potential between a cathode and an anode, introduced into the plasma. The cathode is at a negative potential, \(-\mathbf{V}\), while the anode is grounded. \( V_p \) is the plasma potential. (Adapted from \(^{[21]}\).)

If an item, shielded from ground and other applied potentials, is present in the chamber it is at a negative potential relative to the plasma potential. This phenomenon is also caused by the much faster electrons, which start to build up a negative charge of the object. Electrons are therefore repelled away while ions are attracted. When the electron current and the ion current are equal, i.e. no net current, the object stops from further charging yielding a negative potential. This potential is called the floating potential, \( V_f \).
2.2.2 Diode sputtering

When sputtering is to be used in thin film depositions one normally uses two electrodes, a cathode and an anode. The grounded chamber walls are often used as an anode. Inert gas is then introduced into the chamber. To start the sputtering process a negative potential is applied to the cathode, where the target material is placed. This causes free electrons close to the cathode to accelerate towards the anode. On their way they collide with gas atoms, which are ionized if the kinetic energy is sufficient creating more free electrons according to (2.1).

\[ e^- + Ar \rightarrow 2e^- + Ar^+ \] (2.1)

Once again the electrons are accelerated and more collisions take place, creating an avalanche of ionization events that create and sustain the plasma. Therefore, the plasma consists of ions, electrons and neutrals. The positively charged ions are also accelerated, but instead towards the cathode. As the ions collide with the surface of the target they sputter away atoms that start to coat all surfaces inside the chamber after travelling through the plasma. There are, as discussed earlier in this section, other possible interactions that can take place. One that is of greater importance is the creation of secondary electrons, which further ionize the inert gas and sustain the plasma. All of these interactions heat the cathode, wherefore it is cooled normally using water. Both the target and the cathode can melt if the cooling is insufficient. The sputtering of target atoms goes on as long as the negative potential of the cathode is present.

2.2.3 Magnetron sputtering

To further increase the utilization of secondary electrons in the close vicinity of the target magnets are placed behind as is illustrated in figure 2.2. Target and cathode are then together referred to as a magnetron. This setup traps more electrons close to the target increasing the number of ionization events, which yields more bombarding ions. Therefore, the number of sputtered atoms increase. This implies that it is possible to operate magnetron sputtering at lower pressures and smaller target voltages as compared to diode sputtering.
Electrons and ions in the plasma experience the electric force together with the Lorentz force due to the combined electric and magnetic fields according to (2.2) [21,22,24].

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

where

- \( F \) = force acting on the particle [N]
- \( q \) = charge of the particle [C]
- \( E \) = electric field [V/m]
- \( v \) = velocity of the particle [m/s]
- \( B \) = magnetic field [T]

The above equation implies that the electrons follow different paths depending on the direction of \( v \) relative to both \( E \) and \( B \). If the electric and magnetic fields are parallel to each other the electrons follow a helical path around the magnetic field lines, as long as \( v \) is not parallel to \( B \). They are then only accelerated by the electric field. Of great importance is also the situation that appears where the electric and magnetic fields are perpendicular to each other. This causes the electrons to instead follow a cycloidal motion, returning repeatedly to the surface of the target. Note that this only applies where both fields are present, i.e. in the sheaths. The same kind of motions, but with opposite direction, apply for the ions as well. Due to their much larger mass the radius of the motion is too large.
to affect them inside the chamber. The above-mentioned forces do however not affect atoms since they do not possess any charge.

Since the trapped electrons ionize the gas atoms the efficiency of the sputtering process is higher where the electric and magnetic fields are perpendicular to each other. Consequently, most of the target atoms are sputtered away from this region resulting in the formation of a so-called racetrack. This means that not all of the target material can be utilized.

2.2.3.1 Direct current magnetron sputtering

In direct current magnetron sputtering (DCMS) a constant negative potential is applied to the cathode. This causes atoms to be sputtered away from the target as previously discussed. When the neutral atoms reach the plasma there is a possibility for them to be ionized, for example by a collision with an electron. The degree of ionization of the sputtered atoms is though low in DCMS, typically in the order of a few percents or less \[1,17\]. A larger fraction of ionized particles are though often preferred in many applications for different reasons, e.g. that electric fields can be utilized to control the energy and the trajectories of the ions.

A higher probability of ionization can be accomplished by increasing the plasma density, which is achieved by applying a larger power to the cathode. However, a too large power causes the target to melt due to insufficient cooling. This problem can be overcome by instead employing the technique described in section 2.2.3.2.

2.2.3.2 High power impulse magnetron sputtering

High power impulse magnetron sputtering (HiPIMS) is a deposition technique where high power pulses are applied to the cathode. The pulses possess a duty cycle of less than 10 % and are applied with a frequency lower than 10 kHz \[1\]. This means that it is feasible to apply the same average energy to the cathode as in the case of DCMS, but with a high energy during each pulse. It is therefore possible to obtain high plasma densities without melting the target by utilizing HiPIMS. The ionization degree of the sputtered material has been reported to be as high as 90 % for titanium \[25\]. The higher ionization degree has been demonstrated to allow for filling of \(\mu\)m size trenches \[18\] as well as for off-normal deposition of uniform films \[2,19\]. It has also been shown that the larger ion fluxes enable growth of a columnar structure oriented closer to the substrate normal when deposited at ninety degrees off-normal \[2,16,20\].
2.3 Nucleation and growth

A disadvantage with HiPIMS is that the deposition rate is lower as compared to DCMS. The main reason for this is suggested to be due to that some of the ions are attracted back towards the cathode \cite{17}. If a sputtered atom is (positively) ionized within the cathode sheath region and do not possess sufficient energy to escape, it is just like an argon ion attracted back towards the cathode causing so-called self-sputtering.

2.3 Nucleation and growth

When the sputtered particles have travelled through the plasma they do either get lost to the chamber walls or end up at the position of the substrate where they start to grow a film. The first step in creating a film is when a sputtered atom condenses on the surface of the substrate, then referred to as an adatom. Adatoms are either desorbed back to the plasma without any contribution to the growing film or they diffuse on the surface. Together diffusing adatoms form small clusters, which start to nucleate giving rise to small islands at random locations. The islands grow in size as more adatoms arrive and coalesce with each other when the island density increases.

In most applications the vapor incidents normally to the substrate or at an angle close to the normal. This setup generates a film according to one of the three common growth modes observed in film formation, see figure 2.3. The different growth modes are known as Frank-Van der Merwe (layer by layer), Volmer-Weber (island growth) and Stranski-Krastanov mode, which is a combination of the two others that starts to grow as layer by layer but after a few layers continues to grow as islands. The type of growth mode obtained is determined by the specific surface energies and the kinetic energies of the adatoms \cite{21}.

Figure 2.3: The three basic growth modes for thin films. From left are Frank-Van der Merwe, Stranski-Krastanov and Volmer-Weber shown respectively.
2.3.1 Shadowing effect

If the vapor originates from a source placed on the side of the substrate the sputtered particles instead arrive at an oblique angle with respect to the substrate. The first formed islands create a so-called shadow behind them in the direction of the incoming vapor (figure 2.4a) meaning that no adatoms from the vapor are supplied to the shadowed regions. This causes the film to only continue its growth on the initially formed islands creating separated columns tilted towards the source of the vapor (figure 2.4b). The growth of the columns continue as more material is deposited, but any of them can stop growing at any time if they are shadowed by another column.

![Figure 2.4: Schematic representation of the shadowing effect in thin film growth.](image)

Many times the shadowing effect can be a drawback in film formation, especially when dense coatings on three-dimensional objects are required. Instead the film exhibits a columnar structure with voids in between on the sides of the object that are not facing the target. There are though deposition techniques taking advantage of the shadowing effect to create nanostructured thin films, e.g. glancing angle deposition (GLAD). By utilizing the GLAD technique it is possible to engineer the columnar structure into the shape of e.g. helicals, vertical posts and zig-zag patterns \[3,8,9\] or as a combination thereof \[10\].
Chapter 3

Experimental Details

3.1 Deposition setup

An ultra high vacuum (UHV) chamber was used to perform all depositions. The chamber was equipped with two magnetrons and a substrate holder according to figure 3.1. Occasionally a quartz crystal microbalance (QCM\footnote{The QCM is explained in section 3.2.1} was attached to the chamber.

As it can be seen in figure 3.1, one magnetron was positioned under the substrate, referred to as on-axis, and the other one was placed at ninety degrees with respect to the substrate normal, named off-axis magnetron. The target to substrate distance was about 9 cm for both magnetrons. The QCM was placed directly behind the position of the substrate to monitor deposition rates, but was only attached to the chamber when being used. Before any depositions were performed the chamber was evacuated to a base pressure in the order of $10^{-8}$ Torr, by baking and the use of a turbo molecular pump. Argon, with a minimum purity of 99.9997\%, was used as inert gas for all depositions and was introduced to the chamber through a leak valve. The working pressure was $5.3 \pm 0.1$ mTorr.

3.1.1 Materials and deposition procedure

All depositions were performed on silicon substrates with the dimension $18 \times 18$ mm. The substrates were mounted perpendicular to the surface of the off-axis magnetron where they were held at a constant position throughout the deposition.
Experimental Details

Figure 3.1: Schematic image of the deposition system. Attached to the vacuum chamber are two magnetrons, a QCM and a substrate holder. One magnetron is positioned under the substrate while the other one is placed at ninety degrees. A turbo molecular pump and a leak valve for argon are also part of the system but are not shown in the image.

Prior to deposition they were ultrasonically cleaned in first acetone and then isopropanol, for 5 minutes each, and marked in order to be able to tell which edge that was facing the off-axis magnetron. Furthermore, the substrates were grounded for all depositions in order to investigate if the potential difference between plasma and substrate is sufficient to influence the ions in such a way that the column tilting is affected.

The first step in the deposition procedure was to deposit a seed layer of titanium from the on-axis magnetron for ten minutes in order to increase the adhesion of the final film to the substrate. This was done using DCMS with an applied power of 100 W. The top layer was then deposited from the off-axis magnetron using two different types of materials; copper and chromium. They were mainly chosen due to their difference in adatom mobility, where copper is a high and chromium a low mobility material. In addition, both materials exhibit a high deposition rate as compared to many other metals \cite{26}. All targets were cylindrical with a diameter of 5.08 cm and a thickness of 4 mm.
3.1 Deposition setup

Three different series were deposited using copper. The first one was done using DCMS at different applied powers to study how the deposition rate affects the column tilting. For the two others were HiPIMS employed at different frequencies by first using a constant average power of 200 W in order to investigate the change in column tilting due to the increased portion of ions in the incident vapor. The second of them was performed with a constant average deposition rate for all frequencies to rule out the effect of loss in deposition rate when utilizing HiPIMS as the cause for the change in column tilting. The deposition rates were determined in advance with a QCM and confirmed after deposition with a SEM. Chromium was also deposited using DCMS at different powers to examine the dependency of the deposition rate along with a HiPIMS series with constant average power of 150 W to study the affect of a larger portion of ions on the column tilting. All deposition conditions are summarized in table 3.1. HiPIMS was used with a pulse width of 50 µs at four different frequencies for each set of deposition; 2 kHz, 1 kHz, 500 Hz and 250 Hz. All depositions were made in a random order from a single target. The last deposition for each material was followed by a reference sample.

Table 3.1: Summary of the different series of depositions. HiPIMS was used at four different frequencies for each series; 2 kHz, 1 kHz, 500 Hz and 250 Hz.

<table>
<thead>
<tr>
<th>Material</th>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>DCMS</td>
<td>different powers</td>
</tr>
<tr>
<td>Cu</td>
<td>HiPIMS</td>
<td>constant average power, 200 W</td>
</tr>
<tr>
<td>Cu</td>
<td>HiPIMS</td>
<td>constant average deposition rate</td>
</tr>
<tr>
<td>Cr</td>
<td>DCMS</td>
<td>different powers</td>
</tr>
<tr>
<td>Cr</td>
<td>HiPIMS</td>
<td>constant average power, 150 W</td>
</tr>
</tbody>
</table>
3.2 Analysis

3.2.1 Quartz crystal microbalance

A quartz crystal microbalance (QCM) was used to determine the mass deposition rate of the sputtered material. This makes it possible to acquire the desired thickness of the growing film.

A QCM utilizes a piezoelectric quartz crystal, which starts to oscillate at a resonance frequency when an alternating current is applied. The resonance frequency shifts as the crystal is covered by some additional mass. The change of frequency is directly proportional to the change of mass according to the Sauerbrey equation [27]. Therefore, deposition rate is determined by measuring the frequency of the quartz crystal.

3.2.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is a widely used technique for imaging in materials science. It is a technique capable of producing images with high resolution and large depth of field at the nanometer scale [28]. From these images it is possible to acquire information about surface topography and composition. The only prerequisite is that the samples need to be conductive and vacuum compatible. Images were captured using a LEO 1550 Gemini SEM in this work.

As its name suggests SEM uses electrons with a high energy, which exhibit a shorter wavelength as compared to normal light, to produce an image. A beam of electrons is created in an electron gun, positioned at the top of the microscope, and is accelerated towards the anode, see figure 3.2. The beam continues through the microscope passing electromagnetic lenses, which focus the beam, and a scanning coil, which makes the beam scan the specimen. The beam is then focused to a spot on the surface of the sample by additional electromagnetic lenses.

When the beam of electrons finally strikes the sample, a lot of interactions can take place. The important electron-specimen interactions for imaging in SEM are backscattered electrons and secondary electrons. The choice of detector determines which of the two types of electrons that is to be used to acquire an image. Worth noting is also that X-rays are created when the beam interacts with the specimen. They can be detected to get compositional information about the sample, since each element emits photons with a characteristic energy. One technique utilizing these X-rays is energy-dispersive X-ray spectroscopy (EDX).
3.2 Analysis

3.2.2.1 Backscattered electrons

Backscattered electrons originate from the incoming electron beam. They are reflected back and out from the specimen due to elastic scattering between the electrons and the atoms of the specimen. The incoming electrons are attracted towards the nuclei, changing the trajectory of the electrons. Some of these electrons can be scattered back out from the specimen through additional elastic scattering events and can then be used to create a topographical image. The amount of backscattered electrons depends on the atomic number of the atoms. Heavier atoms backscatter more electrons and therefore appear brighter on the image as compared to lighter atoms. This makes it also possible to obtain compositional images.

3.2.2.2 Secondary electrons

Secondary electrons are due to inelastic scattering between incoming electrons and valence electrons of the specimen atoms. This kind of interaction causes ejection of a valence electron, i.e. a secondary electron. Additional scattering events can also
take place before these electrons leave the specimen. Since secondary electrons are due to inelastic scattering they possess lower energy than backscattered electrons. Electrons with low energy cannot move far in the sample before being recaptured, which means that secondary electrons can only escape from the region close to the surface. Therefore, secondary electrons are thought to be a more surface sensitive signal.

### 3.2.3 X-ray diffraclometry

X-ray diffraction (XRD) is a non-destructive technique that can be used to e.g. determine the texture of the film. In XRD the specimen is irradiated with monochromatic X-rays with wavelength $\lambda$ at varying incident angles $\theta$. The X-rays give rise to constructive interference when being reflected by the specimen if the Bragg equation (3.1) is fulfilled. Therefore, maximum intensity of the reflections is only observed at certain incidence angles for a specific interplanar spacing $d_{h,k,l}$.

$$2d_{h,k,l}\sin\theta = n\lambda, \text{ where } n \in \mathbb{Z} \quad (3.1)$$

The most conventional technique in XRD is the Bragg-Brentano scan also known as the $\theta/2\theta$ scan. It utilizes the same angle on both the incoming X-rays relative to the surface of the specimen and the detector, see figure 3.3. A measurement is made by scanning the angle $\theta$ over a chosen interval while measuring the intensity of the reflections. A disadvantage with Bragg-Brentano measurements is that the lattice planes responsible for the reflections are all parallel or nearly parallel to the surface of the sample.

![Figure 3.3: Schematic illustration of a Bragg-Brentano setup.](image-url)
In order to scan a crystal plane in the film that is not parallel to the surface of the substrate the reflections need to be scanned at different orientations. This is accomplished by keeping the angle $\theta$ at a fixed value corresponding to the desired plane while moving the sample. The sample is tilted in steps and for each step rotated 360° around its normal. The obtained data can then be visualized in a pole figure where the intensity is plotted against the angles of tilting and rotation. Bragg-Brentano measurements and pole figures were obtained utilizing a PHILLIPS X’Pert X-ray diffractometer.

3.3 Definition of the tilting angle

The angle at which the columns are tilted is defined as the angle between the surface of the substrate and the column in this work. It is illustrated as $\theta$ in figure 3.4.

Figure 3.4: The tilting angle of the columns is illustrated as the angle $\theta$ in the figure.
Chapter 4

Results and Discussion

4.1 Copper

4.1.1 Process characteristics

As the frequency decreases the peak target power increases (figure 4.1a). The effect of the peak target power on the deposition rate is shown in figure 4.1b where it can be seen that the deposition rate decreases as the peak target power is increased except for the largest value of the peak target power, which yields a small increase in deposition rate. A larger value of the peak target power has been demonstrated to yield a higher ionization degree of the sputtered material [1]. The loss in deposition rate has been suggested to be due to back attraction of some of these ions towards the target where they self-sputter [17]. It has also been shown that the sputtering yield is a non-linear function (resembles a square root function) of the target potential, which means that the deposition rate is expected to be lower at higher voltages where HiPIMS is operated if a constant average power is used [30]. The self-sputtering yield of metals exhibit the same characteristics and is found to be about 10 - 15 % less than the sputtering yield of argon [31]. For materials with a high self-sputtering yield like copper the plasma can be self-sustained, i.e. no working gas is needed, as the target voltage and hence the self-sputtering yield increases [31]. For such a system it has been shown that the probability of a metal ion to be back-attracted towards the target decreases as the threshold for self-sputtering is passed [32], which implies that the deposition rate increases when operated beyond the threshold [31].
The relationship between deposition rate and applied power in the DCMS process is presented in figure 4.1c. It can be seen that the deposition rate increases as a larger power is applied to the target. Note that due to possible differences in film densities deposition rates are not equal to mass deposition rates.

Figure 4.1: Process characteristics for HiPIMS (a and b) and DCMS (c) of the deposition of copper films. The corresponding deposition rate of DCMS is included as a dashed line in (b). CAP = Constant Average Power, CADR = Constant Average Deposition Rate.
4.1 Copper

4.1.2 Microstructure

The cross-sectional SEM micrographs of two representative copper films grown at constant average power by DCMS and HiPIMS at 250 Hz are shown in figure 4.2. In both images the silicon substrate is seen in the bottom of the image followed by a ∼120 nm seed layer of titanium. On top of the seed layer tilted copper columns are seen. The differences between the two films are that the HiPIMS film (figure 4.2b) is thinner and that its columns are closer to the substrate normal.

![Cross-sectional SEM micrographs of copper films deposited at constant average power using (a) DCMS and (b) HiPIMS at 250 Hz.](image)

(a) Cu, DCMS.  
(b) Cu, HiPIMS 250 Hz.

Figure 4.2: Cross-sectional SEM micrographs of copper films deposited at constant average power using (a) DCMS and (b) HiPIMS at 250 Hz.

The column tilting as extracted from SEM for all frequencies at constant average power and deposition rate are plotted in figure 4.3. It is seen that the angle increases as the frequency is decreased. Note that the angle is measured from the surface of the substrate towards the column. The corresponding value for the DCMS film grown at constant average power is also included in the figure, where the solid line represents its mean value and the two dashed lines the measured range.
4.1.3 Crystallographic properties

Bragg-Brentano scans (figure 4.4) were performed for the copper films shown in figure 4.2. A high intensity silicon peak is observed together with four copper peaks that correspond to the (111), (200), (220) and (311) planes for both samples. The relative intensities of the peaks are listed in table 4.2 together with the corresponding values from the JCPDS card [33]. It can be seen that the (111) peak is dominant for both of the deposited films as well as for the JCPDS card. The relative intensities of the two deposited samples correspond well with each other, but not to the values of the JCPDS card. Since the areas of the peaks are used to calculate the relative intensities it should be noted that the tabulated values can differ some few percentage points depending on how a specific peak is defined.
4.1 Copper

Figure 4.4: Bragg-Brentano measurement for copper.

Table 4.1: Relative intensities of the peaks in figure 4.4

<table>
<thead>
<tr>
<th>Peak</th>
<th>DCMS [%]</th>
<th>HiPIMS [%]</th>
<th>JCPDS [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>30</td>
<td>29</td>
<td>46</td>
</tr>
<tr>
<td>220</td>
<td>12</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>311</td>
<td>13</td>
<td>16</td>
<td>17</td>
</tr>
</tbody>
</table>

No real difference between DCMS and HiPIMS samples are seen in the Bragg-Brentano measurements. It is though possible that the crystal planes are not parallel to the substrate surface due to the off-normal deposition. Therefore, pole figures were measured in addition to the Bragg-Brentano scans.

Pole figures were obtained for the (111) and (200) directions for the same two films that underwent Bragg-Brentano measurements and can be seen in figure 4.5. These planes were chosen since it has been demonstrated that they are typical texture components in copper films [34]. In both of the (111) pole figures (figure 4.5a and 4.5c) one high intensity pole is seen, but an area with a somewhat higher intensity can also be observed above the pole of the DCMS pole figure.
Results and Discussion

The (111) pole of the DCMS film is broader as compared to the one of the HiPIMS film and its peak value is positioned 25° from the centre while the peak value for the HiPIMS film is 5° from the centre. Both of the (200) pole figures (figure 4.5b and 4.5d) demonstrate their maximum intensity on regions around the centre. Note that the direction of the incoming vapor coincides with the zero mark of the pole figures.

Figure 4.5: Pole figures for the (111) (left) and (200) (right) planes for two different copper samples deposited with DCMS (a and b) and HiPIMS at 250 Hz (c and d). Note that the vapor incidents from the zero mark.
4.2 Chromium

4.2.1 Process characteristics

As can be seen in figure 4.6a, the peak target power increases as the frequency is decreased. The increased peak target power causes a reduction of the deposition rate (figure 4.6b). In the case of DCMS (figure 4.6c), the deposition rate increases with an increased power. When compared to the process characteristics of copper in section 4.1.1, it can be noted that the relative loss in deposition rate between the samples with the lowest deposition rate for HiPIMS and the corresponding DCMS value is ~ 30 % for copper and ~ 70 % for chromium. It has been suggested that the larger relative loss in deposition rate of chromium can be due to that its self-sputtering yield is smaller as compared to copper [17].

Figure 4.6: Process characteristics for HiPIMS (a and b) and DCMS (c) of the deposition of copper films. The corresponding deposition rate of DCMS is included as a dashed line in (b).
4.2.2 Microstructure

The cross-sectional SEM micrographs of two representative chromium films deposited at constant average power by DCMS and HiPIMS at 250 Hz are shown in figure 4.7. The silicon substrate can be seen in the bottom of both images followed by the titanium seed layer and on top of that the chromium film. Both chromium films exhibit a columnar structure, where the columns of the DCMS film (figure 4.7a) appear to grow with a dendritic structure. The thickness of the HiPIMS film is smaller as compared to the DCMS film, but no difference in column tilting can be seen.

![Image of SEM micrographs]

(a) Cr, DCMS  
(b) Cr, HiPIMS 250 Hz

Figure 4.7: Cross-sectional SEM micrographs of chromium films grown with (a) DCMS and (b) HiPIMS at 250 Hz.

The tilting angle of the columnar structure as extracted from SEM for all frequencies are shown in figure 4.8. As is seen no difference in tilting angle is observed when changing frequency. The column tilting of the HiPIMS films is the same as for the corresponding DCMS sample, whose mean value is indicated by a solid line in the figure together with the measured range as dashed lines.
4.2 Chromium

Figure 4.8: Column tilting as a function of frequency. The mean value for the DCMS film is included as a solid line together with the measured range as dashed lines.

4.2.3 Crystallographic properties

Bragg-Brentano scans were performed for the two films grown at constant average power by DCMS and HiPIMS at 250 Hz and can be seen in figure 4.9. Chromium peaks that correspond to the (110) and (211) planes are seen together with the intense silicon (400) peak for both samples. The intensity of the peaks that belongs to the DCMS film is slightly larger. The relative intensities of the peaks can be seen in table 4.2 together with the corresponding values of the JCPDS card for chromium [35]. The (110) peak is dominant for all three tabulated samples and for the two deposited films no (200) peak can be seen. Neither of the samples are found to coincide with each other.
Figure 4.9: Bragg-Brentano measurement for chromium.

Table 4.2: Relative intensities of the peaks in figure 4.9

<table>
<thead>
<tr>
<th>Peak</th>
<th>DCMS [%]</th>
<th>HiPIMS [%]</th>
<th>JCPDS [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>211</td>
<td>4</td>
<td>26</td>
<td>30</td>
</tr>
</tbody>
</table>

Pole figures were measured for the (110), (200) and (211) directions for the same two films that Bragg-Brentano measurements were performed on. The intensities of the (211) pole figures were very low, therefore only the results from the (110) and (200) pole figures are presented in figure 4.10. A central pole surrounded by four other poles situated 60° away from the centre is seen for the (110) pole figure of the DCMS film (figure 4.10a). The corresponding (200) pole figure (figure 4.10b) consists of two intense poles 45° from the centre and two poles with a lower intensity located 40° and 50° from the centre respectively. The (110) pole figure of the HiPIMS film (figure 4.10c) is very much different with a much lower intensity. It consists of only two distinct poles positioned 25° degrees from the centre, but an area with a somewhat higher intensity can also be seen above the
two poles. The corresponding (200) pole figure (figure 4.10d) exhibits a very low intensity and two broad poles that almost form a ring around the centre. The two poles are situated 40° and 50° away from the centre respectively. As for the pole figures of copper the direction of the incoming vapor coincides with the zero mark of the chromium pole figures.

![Figure 4.10: Pole figures for the (110) (left) and (200) (right) planes for two different chromium samples deposited with DCMS (a and b) and HiPIMS at 250 Hz (c and d). Note that the vapor incidents from zero.](image_url)
4.3 Discussion

To better understand the affects on the column tilting when changing frequency the tilting angle is plotted as a function of the peak target power in figure 4.11. A larger value of the peak target power has been demonstrated to yield a larger portion of ions in the incident vapor [1]. It is seen that the tilting angle increases with increasing peak target power and hence a larger ion to neutral ratio for copper. One explanation for this is that the trajectories of the ions are deflected towards the substrate normal as they enter the sheath, as has been suggested in the literature [2,16,20]. Therefore, they are deposited at an angle closer to the normal raising the columns. Furthermore, since adatoms diffuse from regions with high concentration (the tip) towards areas with low concentration (the shadowed region) [3] an increase of surface mobility caused by the larger amount of bombarding ions present in HiPIMS can also raise the columnar structure. The same result is not observed for chromium, where all deposited films exhibit the same tilting angle.

![Figure 4.11: Column tilting as a function of peak target power for copper and chromium. Mean values for the films grown by DCMS at the corresponding constant average power are marked with solid lines together with the measured range as dashed lines. CAP = Constant average power, CADR = Constant average deposition rate.](image-url)
Another factor that affects diffusion is the deposition rate. This is because a larger deposition rate causes adatoms to be capped more rapidly decreasing the diffusion length and resulting in columns tilted farther away from the substrate normal \[13,14\]. The tilting angle is plotted as a function of the deposition rate in figure 4.12. Small differences in the column tilting can be seen for DCMS films as well as for HiPIMS films, but the affect of the peak target power is more pronounced. Therefore, the peak target power is the decisive factor of the tilting angle.

![Graph showing column tilting as a function of deposition rate for copper. CAP = Constant average power, CADR = Constant average deposition rate, DP = Different powers.](image)

Figure 4.12: Column tilting as a function of deposition rate for copper. CAP = Constant average power, CADR = Constant average deposition rate, DP = Different powers.

The pole figures of copper (figure 4.5) demonstrate that both the DCMS film and the HiPIMS film exhibit a fiber texture with an [111] out of plane orientation. A schematic representation of the corresponding unit cell is given in figure 4.13a. The (111) planes are also the lowest surface energy planes for copper and are expected to grow with the out of plane orientation \[36\]. The position of the peak value for the (111) pole figure of the HiPIMS film (figure 4.5c) is closer to the centre as compared to in the DCMS film (figure 4.5a). This means that the (111) planes of the HiPIMS film are closer to be parallel with the substrate surface. The difference in peak position is \(\sim 20^\circ\), which is in good agreement with the
\(\sim 15^\circ\) difference in column tilting measured by SEM. A likely explanation to the
shift of peak position is therefore that the tilting of the columnar structure differs.
Furthermore, the broadening of the peak is smaller for the film deposited with
HiPIMS. This implies that the columns of the HiPIMS film deviate less from the
average tilting value and/or that the crystal planes are more aligned with each
other.

Figure 4.13: Schematic representation of (a) fiber texture with [111] out of plane
orientation and (b) biaxial texture with [110] out of plane orientation. The base
plane is marked in each figure. All facets correspond to (200) planes.

The chromium pole figures of the DCMS grown film (figure 4.10a and 4.10b)
imply a biaxial texture with an [110] out of plane orientation. A schematic rep-
resentation of the corresponding unit cell is given in figure 4.13b. The two less
intense poles of the (200) pole figure suggest that some of the grains are rotated
90° with respect to each other. HiPIMS pole figures (figure 4.10c and 4.10d) also
propose a certain degree of biaxial texture with [110] out of plane orientation,
where the two poles of the (110) pole figure suggest that two biaxial alignments
are present.

A large difference in the tilting angle of the columnar structure between copper
and chromium is observed and can be seen in for example figure 4.11 or the cor-
responding SEM images (figure 4.2 and 4.7). One of the characteristic differences
between copper and chromium is the adatom mobility, where copper is a high and
4.3 Discussion

chromium a low mobility material. Therefore, it is somewhat contradictory that the copper columns tilt further away from the substrate normal as compared to the chromium columns since an increased mobility of a single material has been demonstrated to raise the columnar structure \[11,12\]. Different degrees of mobilities have also been demonstrated to yield differences in the nucleation process, where higher mobility materials like copper are expected to grow larger and less islands for the same substrate coverage as compared to low mobility materials like chromium \[37\]. Copper also exhibits a larger sputtering yield, which means that larger growth rates can be expected \[1\].

The differences in size and shape of the initially formed islands between copper and chromium might introduce differences in the amount of shadow falling on a single island. A smaller distance between islands (as in the case of low mobility materials) would lead to that a larger fraction of a single island is shadowed as depicted in figure \[4.14\]. The islands would then only be able to continue their growth on the top most part, which would cause them to grow more towards the direction of the substrate normal as compared to high mobility materials. If this is a valid explanation for the observed difference in column tilting angle between copper and chromium or not is not known and need to be investigated further.

![Diagram](image)

Figure 4.14: Schematic representation of the initially formed islands and the corresponding shadow (upper part) for (a) a high mobility material and (b) a low mobility material together with how the growth evolves (lower part). Note that the vapor incidents from the right side.
The large difference in tilting between copper and chromium can also be an explanation to why no difference in column tilting is observed for chromium as the peak target power increases. Since the columnar structure of chromium is closer to the substrate normal almost all the incident particles would need to arrive along the substrate normal to be able to raise the columnar structure. The grounded substrates might not be enough to sufficiently deflect the trajectories of the ions in such a way that they arrive normal to the substrate. Consequently, no difference in column tilting can be observed.
Chapter 5

Summary

This work was carried out in order to increase the knowledge of the off-normal growth process when employing HiPIMS. Thin films of copper and chromium were deposited on grounded substrates orthogonal to the target at various pulsing frequencies. Samples were also grown using DCMS, which were used as reference with a low ionization degree. Before the final film was deposited a titanium seed layer was grown to increase the adhesion of the film with the substrate. The cross-sectional views of all films were investigated using SEM where the tilting angle of the columnar microstructure was measured together with the film thickness. Furthermore, the films corresponding to the highest and lowest ionization degrees were analyzed using XRD to investigate how the crystal planes are influenced by the larger amount of ions in the incident vapor.

It is shown that the columnar structure of the copper films tilts less with respect to the substrate normal as the peak target power increases, corresponding to a higher degree of ions in the incident vapor \[1\]. One explanation to this is that the trajectories of the ions are deflected towards the substrate and therefore the ions are deposited at an angle closer to the normal, as has been suggested in the literature \[2,16,20\]. Energetic bombardment by ions can also increase surface mobility, which further raises the columnar structure. It is also concluded that the difference in column tilting is not caused by a lower deposition rate obtained when utilizing HiPIMS. The same is not observed for chromium, which yields the same tilting angle for all samples.

A large difference in column tilting between copper and chromium samples is also observed. The columns of chromium stand closer to the substrate normal
as compared to the ones of copper. One characteristic difference between copper and chromium is the surface mobility, where copper is a high and chromium a low mobility material. Another one is the surface energy, where copper exhibits a lower surface energy than both chromium and the underlying titanium seed layer while the value of chromium is the largest of them. Both of these differences might affect nucleation and growth, but it is not known if and how they affect the tilting of the columnar structure. Therefore, further investigations are needed in order to be able to explain the observed difference in column tilting between copper and chromium.

Furthermore, it is revealed that the copper films exhibit a fiber texture with an [111] out of plane orientation. The grains of the HiPIMS films are better aligned with each other and are also found to be oriented closer to the substrate normal as compared to the DCMS films. For chromium, a certain degree of biaxial texture with an [110] out of plane orientation is observed for both DCMS and HiPIMS grown films.
Chapter 6

Future Outlook

There are a lot of possible and interesting works that can be performed to increase the knowledge of how the off-normal growth is determined, focusing on the difference between materials. Some alternatives are discussed in the following text.

It would be interesting to study even more materials with different degrees of surface mobilities to see if any general conclusion can be made regarding kinetics and its impacts on the column tilting. The affects of using seed layer is another thing that need to be clarified. The question is if the choice of seed layer or the use of no seed layer affects the growth and more interestingly how. More investigations through depositions and nucleation studies are needed to be able to tell why a difference in column tilting is observed. Another interesting approach would be to deposit different materials at the same homologous temperature to see if and how the column tilting is affected.

Characterization of the plasma at the position of the substrate might also give valuable information to further understand the off-normal growth. To perform a systematic investigation of how the off-normal growth process is affected when different bias voltages are applied would also be worth looking into.
Bibliography


[33] JCPDS-ICDD, 04-0836 for cubic Cu.


[35] JCPDS-ICDD, 06-0694 for cubic Cr.
