Kinetic Monte-Carlo studies of island shape evolution on weakly-interacting substrates

Filip Thunström

Examiner, Kostas Sarakinos
Supervisor, Victor Gervilla
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Sammanfattning

Metal thin films deposited on weakly-interacting substrates constitute an essential element of numerous microelectronic, catalytic, and optical devices. However, the natural tendency of metal atoms to agglomerate, upon condensation on a weakly-interacting surface, in dispersed three-dimensional (3D) islands affects negatively the performance of the above-mentioned devices. The aim of this thesis is to investigate one of the mechanisms governing silver (Ag) 3D island growth on weakly-interacting substrates, i.e. the nucleation of a new layer on the island top. Kinetic Monte Carlo (KMC) simulations are employed to calculate the top island-layer critical radius $R_c$ required for nucleating a new layer in the out-of-plane direction. Single-island simulations are performed for growth temperatures $T$ in the range 250 to 500 K and ratios of the pairwise adatom/substrate atom bond strength $E_{B,sub}$ to the corresponding adatom/adatom value $E_{B,lim}$ in the range 0.5 to 0.75. We find that for $T$ values below 250 K the islands exhibit a 2D morphology for all $E_{B,sub}/E_{B,lim}$ ratios. In contrast, for $T$ values above 300 K there exists a range of relatively small $E_{B,sub}/E_{B,lim}$ values, where 2D morphology dominates. To calculate $R_c$ for each island layer as the island shape evolves, a subroutine is developed and implemented in an existing KMC algorithm. $R_c$ values are computed for 3D island growth at $E_{B,sub}/E_{B,lim} = 0.5$ in the $T$ range 300–500K and the results show that $R_c$ decreases monotonously from 17.3 to 6.0 Å and saturates approximately at 375 K. This trend is opposite to the typical behavior of islands grown under homoepitaxial conditions, for which the enhancement of downward inter-layer diffusion caused by an increase of $T$ leads to lower atomic densities on the top, i.e.to a lower nucleation probability, and thus to an increase of $R_c$. This work contributes to the understanding of the physical processes that control thin-film morphological evolution; which is paramount for controlling and manipulating film growth for specific applications.
Abstract

Metal thin films deposited on weakly-interacting substrates constitute an essential element of numerous microelectronic, catalytic, and optical devices. However, the natural tendency of metal atoms to agglomerate, upon condensation on a weakly-interacting surface, in dispersed three-dimensional (3D) islands affects negatively the performance of the above-mentioned devices. The aim of this thesis is to investigate one of the mechanisms governing silver (Ag) 3D island growth on weakly-interacting substrates, i.e. the nucleation of a new layer on the island top. Kinetic Monte Carlo (KMC) simulations are employed to calculate the top island-layer critical radius $R_c$ required for nucleating a new layer in the out-of-plane direction. Single-island simulations are performed for growth temperatures $T$ in the range 250 to 500 K and ratios of the pairwise adatom/substrate atom bond strength $E_{B,\text{sub}}$ to the corresponding adatom/adatom value $E_{B,\text{film}}$ in the range 0.5 to 0.75. We find that for $T$ values below 250 K the islands exhibit a 2D morphology for all $\frac{E_{B,\text{sub}}}{E_{B,\text{film}}}$ ratios. In contrast, for $T$ values above 300 K there exists a range of relatively small $\frac{E_{B,\text{sub}}}{E_{B,\text{film}}}$ values, where 2D morphology dominates. To calculate $R_c$ for each island layer as the island shape evolves, a subroutine is developed and implemented in an existing KMC algorithm. $R_c$ values are computed for 3D island growth at $\frac{E_{B,\text{sub}}}{E_{B,\text{film}}}=0.5$ in the $T$ range 300 – 500 K and the results show that $R_c$ decreases monotonously from 17.3 to 6.0 Å and saturates approximately at 375 K. This trend is opposite to the typical behavior of islands grown under homoepitaxial conditions, for which the enhancement of downward inter-layer diffusion caused by an increase of $T$ leads to lower atomic densities on the top, i.e. to a lower nucleation probability, and thus to an increase of $R_c$. This work contributes to the understanding of the physical processes that control thin-film morphological evolution; which is paramount for controlling and manipulating film growth for specific applications.
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Chapter 1

Introduction

Thin films are solid materials, with thicknesses ranging from a few atomic layers to several micrometers, which are deposited on an object (substrate) to alter or improve its properties. The properties of a thin film may differ from those of the bulk material, since the substrate imposes a structural order on the deposited film. Common applications of thin films are protective coatings on tools to increase their durability, optical coatings e.g. on solar panels to decrease their reflectivity, and decoration. By adjusting different parameters during the deposition process such as temperature and deposition rate, it is possible to control growth in order to achieve thin films with specific properties.

Metal thin films on weakly-interacting substrates (hereafter referred to as WIS) are essential in microelectronic components and in catalytic applications. They can also be used for reducing the radiation emission of windows. However, the natural tendency of metals deposited on WIS to agglomerate in isolated 3D islands affects the final microstructure and roughness of the film, which has a negative impact on its electrical conductivity and consequently on its performance in the above-stated applications. In this way, understanding the microscopic phenomena responsible for the 3D growth is a key step towards the production of thin and conductive high quality films. Experimentally, it is difficult to investigate the atomistic mechanisms involved during thin film growth, since they occur on small length- (≤ Å) and timescales (≤ ns). With computer simulations implementing theoretical models, however, it is possible to obtain a better picture of the detailed processes. The kinetic Monte Carlo (KMC) method is well suited for this purpose, and has been widely used to study thin film growth since it allows for simulating the time evolution of a system over relatively large, close to realistic, length- and timescales.

Observations based on growth simulations and experiments suggest that islands forming from deposited atoms grow preferentially in-plane up to a critical radius. It has been shown that when the radius of the top of the islands becomes larger than a critical value $R_c$, the top-layer nucleation probability increases rapidly, allowing 3D growth to take place [11]. Despite its conceptual simplicity, this hypothesis has not been confirmed for islands grown in WIS. On a WIS upwards mass transport from the substrate to the island top constitutes an additional source for the adatom density on the island top, compared to metal-on-metal epitaxy where direct deposition is the only source of free adatoms to the top. In this project we investigate the dynamic processes occurring on the top island layer and attempt to find a connection between...
the probability of top-layer nucleation of the islands and its radius, i.e., to calculate $R_c$. The project entails understanding of the KMC algorithm and the physical model, its implementation in a simulation code and modification of this code in order to study in detail dynamic properties on top of the islands. The research question that this thesis answers is how $R_c$ depends on deposition conditions and its connection with island shapes and film morphology.

To investigate this problem an existing in-house developed KMC code (hereinafter UniKMC) which implements the KMC algorithm for simulating thin film growth of Ag on weakly-interacting substrates was used. Supercomputer resources at NSC were used for running the simulations. A subroutine was devised and implemented in UniKMC, that calculates the critical radius for each layer during the evolution of an island. The top-layer critical radius $R_c$ was calculated for temperatures between 300 K and 500 K at a pairwise bond strength between Ag and substrate atoms set to 50% of the corresponding Ag-Ag value, averaging over the results of five independent single-island growth simulations for each temperature. It was shown that the average critical radius decreases from $\sim 17.3$ Å to $\sim 6$ Å when increasing the temperature from 300 K to 375 K, until it reaches a steady state value of $\sim 6$ Å from 375 K to 500 K.

This project is a direct continuation of previous research by Bo Lü et al. [3] [7] [8] [9] [10] [11] in the Nanoscale Engineering Division at IFM, Linköping University, where both experiments and computer simulations were employed to investigate the microscopic processes involved in island nucleation, growth and coalescence, and their dependence on vapor deposition rate and substrate temperature. Simulation software implementing an atomistic model for Ag on weakly-interacting substrates was developed, which helps to identify the atomic-scale processes that take place during the evolution of the islands, which has contributed to the understanding of how 3D island growth takes place at the atomic scale.

The thesis is organized as follows. In Chapter 2 thin film theory and the KMC algorithm are described. Chapter 3 treats the theoretical approach, where the simulation software, UniKMC, is described, as well as how the critical radius was defined in this project, a description of the subroutine and the simulation strategy. In Chapter 4 the simulation results are presented and discussed and in Chapter 5 the overall results are summarized. Appendix A includes flow charts which illustrate the functioning of the subroutine. Appendix B describes how statistics were calculated.
• Chapter 2

Theory

2.1 Formation of thin films

A thin film is formed from the vapor phase by deposition of atoms on a substrate, which then may find each other and form islands (an island is a cluster of two or more atoms supported by a surface). During the early stages of growth many nucleation events (island formations) occur, in the film formation stage known as nucleation. Depending on the growth conditions the islands may then meet either as a result of the islands being mobile enough so that they can move around and impinge on each other, or as a result of the growth of the islands. Two islands that meet will merge and form a larger island, which will result in a decrease of the island density. This growth stage is called coalescence. Later on, islands start impinging on coalescing clusters which has not completed the merging process, forming thus elongated structures. This morphological transition is defined as the elongation transition. When the coverage is great enough so that most islands are connected to each other across the surface forming a continuous network, the percolation transition has been reached. For metal thin films on WIS, it is possible to determine the time at which the percolation transition takes place by measuring the onset of electrical conductivity of the film. For further coverage, holes in the percolation network are filled to form a continuous film. See figure 2.1 for illustrations.

![Figure 2.1: The growth stages during film formation.](image)
2.2 Surface diffusion

Before an adatom arrives to the surface, it is accelerated within the attractive potential of the surface and acquires a certain kinetic energy $E_{\text{kin}}$ [12]. Upon arrival, in order to stick at the surface rather than escaping from it, it has to dissipate enough of its energy to the crystal lattice, i.e. the energy of the atom has to be placed below an adsorption energy $E_{\text{ad}}$ to be adsorbed on the surface. If adsorption is successful, the atom is defined as an adatom. The probability for an incoming atom to be adsorbed at the surface is represented by a sticking coefficient.

When an adatom has been adsorbed at the surface, it starts diffusing if its kinetic energy is sufficiently high. Surface diffusion of adatoms is a fundamental factor for the evolution of a thin film, and can often be described classically, although for very light adatoms quantum mechanical effects may contribute significantly to the diffusion process [12]. Atoms have been shown to diffuse both via direct hopping from one site to another and via an exchange mechanism, which was discovered using density functional theory calculations in 1990 [12] [16]. Unlike in regular hopping, in an exchange diffusion event an atom dives into a local environment, taking the place of another atom and pushing it to another site on the surface, in a way so that the original adatom appears to have moved across the surface.

When an adatom diffuses on the substrate it can encounter other adatoms to form a dimer. It can also encounter an island, diffuse along its edges and be incorporated into its steps and kinks, or cross the step of the island and ascend to a higher layer, or if it already is on an island, it may descend to a lower layer (see figure 2.2 which illustrates some possible ways an adatom may move). An adatom is most likely to attach to a step or a kink, since they have a high coordination number, i.e. a stable position with a large amount of bonds, which implies that a high amount of energy is needed for the adatom to escape from those positions.

The rates at which adatoms diffuse to new occupation sites are calculated via the Arrhenius equation,

$$\nu = \nu_0 e^{-\frac{E_D}{k_B T}}$$

(2.1)

where $\nu_0$ is the attempt frequency, $E_D$ is the activation energy for diffusion between two sites on the surface, $k_B$ is Boltzmann’s constant and $T$ is the temperature. It follows that the jump rate increases with increasing temperatures and for decreasing energy barriers. $E_D$ depends on the energy difference between the atoms initial position and the saddle point (the transition state) between the initial position and the final position in the corresponding energy landscape, see figure 2.3. $\nu_0$ is a measure for the time scale in an infrequent-event system, i.e. adatoms spend long times in their lattice sites between jumps, before they acquire sufficient kinetic energy to make a successful jump to a neighboring site. $\nu_0$ can be interpreted as the vibration frequency of the atomic lattice, since lattice vibrations in the substrate and in the film may provide enough energy for an atom to diffuse from its current position to a neighboring position [12].

When an adatom diffuses to a higher or a lower layer of an island it has to cross a step, a process for which the adatom has to overcome an additional activation barrier known as the ES
Figure 2.2: Sketch of a few atomic processes. Atom 1 may diffuse along the step edge or detach from it, atom 2 is incorporated in a *kink* but may diffuse along the step edges, atom 3 may nucleate or diffuse along the surface, atom 4 diffuses on a terrace.

Figure 2.3: An adatom diffusing across a surface and its corresponding energy landscape. The energy landscape describes how strongly bound the adatom is to neighboring atoms. When in a potential energy well, the adatom needs at least a sufficient energy $E_D$ in order to diffuse to another position.
barrier (Ehrlich–Schwoebel barrier). This barrier arises from the fact that when the adatom diffuses across the step, the length of the jump is relatively long because it has to pass through an area with a low number of nearest neighbors, where it will be weakly bound, before arriving to a site with a higher coordination number, where it is more strongly bound. See figure 2.4 for an illustration of the energy landscape at and near a step. This additional energy barrier $\Delta E_S$ is described by

$$\Delta E_S = E_S - E_D$$  \hspace{1cm} (2.2)$$

where $E_S$ is the activation barrier for a step adatom to ascend to the upper layer. It affects the energy landscape near a step by increasing the energy barrier that an atom has to overcome when descending or ascending across a step [5]. The ES-barrier determines the rate of interlayer transport, i.e. the rate of transport of atoms between different layers. It has been observed that a large step-edge barrier increases the time that adatoms reside on top of an island, and by extension the probability of nucleation of a next layer, since two atoms that are present on the same layer simultaneously are more likely to meet if it is difficult to diffuse off it. The step may also induce long range distortions of the surface lattice, which may affect the movement of adatoms long before they reach the step [12].

In this work fcc (111) surfaces with hexagonal symmetries are investigated, see figure 2.5 for an illustration of the different types of sites and edges. Two different types of lattice sites are possible for an adatom to be adsorbed at: if it is adsorbed at an fcc (face centered cubic) site it continues the fcc structure of the substrate, and if it is adsorbed in an hcp (hexagonal close packed) site it starts a new hcp structure. Fcc-sites are more energetically favourable than
hcp-sites, and therefore the nucleation probability is higher in fcc sites [12]. It has been shown that for deposition of Ag on a Pt(111) surface at 45 K, adatoms that were adsorbed at hcp-sites at first, hop to fcc-sites at a high rate compared with that of a regular fcc-fcc diffusion jump [12].

2.3 Atomistic nucleation theory

The atomistic nucleation theory explains the formation of islands via the rates of individual atoms attaching to and detaching from islands of different sizes. It is a statistical approach for describing the early stages of film growth and has been used for calculating jump rates $v_0$ and activation energies $E_D$ from data of island number densities obtained from experiments. From making certain assumptions, analytical expressions for the relations between island number density and deposition parameters can be found.

The development of atomistic nucleation theory was necessary in order to understand far from equilibrium growth where the stable nucleus may reach atomic sizes and thermodynamic theory can not be easily applied. The growth taking place far from equilibrium is caused by supersaturation of the vapor, i.e. the vapor pressure is high compared to the vapor pressure at room temperature due to the growth taking place at higher temperatures. Thermodynamically it means that there is a driving force for deposition, a difference in chemical potential (pressure) between the vapor phase of the deposit and the substrate. The atomistic nucleation theory has been thoroughly tested, experimentally and with computer simulations.

The classical, analytical approach to the kinetics of nucleation begins with rate equations for the number of clusters per surface area $n_s$ for clusters consisting of $s$ atoms. This means that
the density \( n_1 \) of adatoms, \( n_2 \) of dimers (an island consisting of two atoms), and so on are considered. It is assumed that only adatoms can move on the surface and that the mobility of clusters can be neglected, so that existing clusters can only grow by capturing adatoms. The rate equations describe how the density of clusters of different sizes \( s \) varies with time as a function of deposition rate, the rates at which \( s+1 \) clusters form from \( s \)-clusters etc. The deposition rate is usually measured in monolayers per second (ML/s). One monolayer is a measure of the amount of atoms needed to cover the entire substrate with atoms in a close packed manner \[14\]. The net formation rates \( \Gamma_s \) which describe the net rate that \( s + 1 \) clusters form from \( s \) clusters can be expressed as

\[
\Gamma_s = \sigma_s D n_1 n_s - \gamma_{s+1} n_{s+1} \quad (2.3)
\]

where the capture number \( \sigma_s \) describes the probability of how likely a cluster is to capture adatoms depending on the size of the cluster, as well as on the size and locations of nearby clusters and \( \gamma_s \) is the rate that adatoms detaches from clusters of sizes \( s \) at. The first term in equation 2.3 accounts for the capture of new adatoms to form clusters of size \( s + 1 \) from clusters of size \( s \) \[14\]. The second term accounts for the decay of clusters of size \( s + 1 \) that form \( s \) clusters. When \( \Gamma_s = 0 \), the formation rate of islands of size \( s + 1 \) from islands of size \( s \) does not change with time, and a local equilibrium has been established. The change in the density of islands of size \( s \) with time can then be expressed as difference between the net formation rates of islands of sizes \( s - 1 \) and \( s \) as

\[
\frac{dn_s}{dt} = \Gamma_{s-1} - \Gamma_s \quad (\geq 2) \quad (2.4)
\]

By neglecting the desorption of adatoms from the surface so that the density of adatoms can only decrease as a result of them being adsorbed by dimers or by larger islands, the adatom rate equation can be described as

\[
\frac{dn_1}{dt} = F - 2\Gamma_1 - \sum_{s \geq 2} \Gamma_s \quad (2.5)
\]

It is here necessary to distinguish between stable and unstable clusters, by introducing a critical cluster size \( i^* \). This distinction is needed because the equations 2.3 - 2.5 contain too many unknown kinetic parameters otherwise. In order to form an atomic layer on a high symmetry substrate without steps or defects, mobile adatoms must meet and form stable clusters \[12\]. \( i^* \) is related to the free energy barrier that has to be overcome for an island to reach the stable phase, where it does not dissolve. If a cluster has a size \( s \) greater than \( i^* \), i.e. if \( s + 1 \geq i^* \), then the cluster is considered to be stable and is assumed to not decay, while unstable clusters decay as a result of detachment of adatoms fast enough so that thermodynamic equilibrium is reached between the different cluster size populations, e.g. adatoms may detach from dimers at the same rate at which dimers capture adatoms, so that the number densities of adatoms and dimers remains constant. It is important to point out that the notion of a critical nucleus size is somewhat artificial, because in reality atoms can detach from clusters of any size. The total density \( N \) of stable clusters can then be described as
\[ N = \sum_{s=i+1}^{\infty} n_s \]  

(2.6)

From these relatively simple, probabilistic assumptions, what is known as the central result of nucleation theory can be derived. This result consist on a scaling relation between the island density \( N \), the deposition rate \( D \) and substrate diffusivity

\[ N \sim \left( \frac{F}{D} \right)^\chi, \chi = \frac{i^*}{i^* + 2} \]  

(2.7)

This expression can be used for calculating the activation energy and attempt frequency for surface diffusion using data from experimental observations of island densities. Experiments should be performed at low temperatures, for the dimers to be immobile and unlikely to decay. The activation energy \( E_D \) and the prefactor \( D_0 \) can be calculated via a linear fitting of the logarithm regression of the Arrhenius equation where the independent variables are \( \ln(N) \) and \( 1/T \),

\[ N = Ce^{E_D/3k_BT} \implies \ln(N) = -\frac{E_D}{3k_BT} + \ln(C) \]

C is a prefactor containing \( \nu_0 \), see [12] for more details. Thus, by calculating the slope of the line \( E_D \) is obtained, and from the intercept of the line with the \( \ln(N) \) axis \( D_0 \) (or the attempt frequency \( \nu_0 \)) is calculated. The theory can also be applied for understanding the energetics of the bonding between surface atoms.

It is important to note that atomistic nucleation theory is only valid in the submonolayer regime since direct impingement and coalescence of clusters have been neglected. Experiments therefore have to fulfill certain criteria in order for atomistic nucleation theory to be applicable, such as the absence of interactions between adatoms, no mobile dimers and no contaminations which can be difficult to achieve. Therefore it is convenient to use computer simulations to calculate energies, since the simulation code can be modified in order to simulate an ideal system in which the approximations made in atomistic theory holds.

### 2.4 Second layer nucleation theory

If second layer nucleation begins after island coalescence, the first layer is completed before higher layers have grown significantly, and the exposed surface at one monolayer (ML) coverage is almost perfectly flat. This growth mode is known as layer-by-layer (LBL) growth, which is characterized by island nucleation on terraces, and the incorporation of adatoms into island steps (see figure 2.6). LBL growth at high temperatures indicates that there is interlayer transport (i.e. adatoms have enough kinetic energy to diffuse down). On the other hand, second layer nucleation occurring before the impingement of the first layers of the islands leads to substrates partially covered by isolated multilayer islands [12].
Attempts to describe second layer nucleation using rate equations have been proved unsuccessful. However, a simple probabilistic model developed by Krug et al. [5] can account both qualitatively and quantitatively for this phenomenon. This model is constructed by defining three relevant time scales for second layer nucleation, which here are specified for the case of a circular 2D island with a fixed radius \( R \). Atoms are deposited onto the island with a flux \( F \). These time scales are the mean time interval between subsequent arrivals of atoms on the islands

\[
\Delta t = \frac{1}{F \pi R^2} \tag{2.8}
\]

the time needed for an atom to diffuse across the island

\[
\tau_D \approx \frac{R^2}{D} \tag{2.9}
\]

and the mean residence time that an atom spends on the island if no nucleation occurs

\[
\tau = \bar{n}/F = \frac{R^2}{8D} + \frac{R}{2a
'} \tag{2.10}
\]

where \( \bar{n} \) is the spatially averaged adatom density on the island, calculated assuming steady-state conditions. Here \( \nu' \) is the interlayer hopping rate (calculated with the Arrhenius equation 2.1) and \( a \) is the nearest neighbor distance between atoms. The first term in eq. 2.10 dominates in the weak barrier regime, i.e. when the ES-barrier is low, and the residence time \( \tau \) is on the same timescale as the diffusion time, since the adatom will most likely leave the island after diffusing across it a few times. For the strong barrier regime the second term dominates, because the adatom diffusion rate becomes negligible and \( \tau \) depends mainly on the rate of interlayer transport.

For a second layer to form, at least two adatoms must populate the island top simultaneously and meet when both atoms are still present on the island [12]. Thus, if the ES barrier is strong, the two atoms have a very high probability of meeting. This nucleation probability can be computed taking into account that deposition is a Poisson process, and therefore it can be represented with an exponential distribution of mean \( \Delta t \). In this way, the arrival time of an atom to the top of the island is described by an exponential random variable \( t \). In order to calculate the probability that two adatoms meet on the island top, the time at which the first
atom arrives on the island is defined at $t = 0$, the time it leaves the island is defined as $t_1$, and the time when the second atom arrives on the island top is defined as $t_2$. Therefore, in order for the two adatoms to have a chance to meet, the time $t_1$ must be greater than $t_2$, and the probability for this to occur is calculated as

$$
Prob[t_1 > t_2] = \frac{1}{\Delta t} \int_0^\infty dt_1 P_{res}(t_1) \int_0^{t_1} dt_2 e^{-t_2/\Delta t}
$$

(2.11)

where $P_{res}$ is the distribution of residence times, and it is assumed that the mean residence time of an adatom on the layer is much less than the time between arrivals of new adatoms, $\tau \ll \Delta t$, which holds under typical growth conditions. Using this assumption, the time between the first adatom arriving at a time $t = 0$ and departing at a time $t_1$, which is its residence time, is much shorter than the time between the time $t = 0$ and the time $t_2$, so that $t_1 \ll \Delta t$. Then $t_1$ in the first integral is effectively integrated from time $t = 0$ to $t = \Delta t$. Then, since $t_2$ is integrated from 0 to $t_1$, $t_2 \ll t_1 \ll \Delta t$. Thus, the second integral in equation 2.8 can be calculated as

$$
t_2 \ll \Delta t \implies \frac{t_2}{\Delta t} \ll 1 \implies e^{-\frac{t_2}{\Delta t}} \approx 1
$$

$$
\implies \int_0^{t_1} dt_2 e^{-\frac{t_2}{\Delta t}} \approx \int_0^{t_1} dt_2 = t_1
$$

Then $Prob[t_1 > t_2]$ can be calculated as

$$
\tau \ll \Delta t \implies t_1 \ll \Delta t \implies
$$

$$
Prob[t_1 > t_2] \approx \frac{1}{\Delta t} \int_0^\infty t_1 P_{res}(t_1) dt_1 = \frac{1}{\Delta t} \int_0^{\Delta t} t_1 P_{res}(t_1) dt_1 = \frac{\tau}{\Delta t}
$$

Since

$$
E(X) = \int_{-\infty}^{\infty} xf(x)dx
$$

from probability theory, where $E(X)$ is the mean value of $X$ and $f(x)$ is the probability density of $X$, and the fact that $\tau$ is the mean residence time and much shorter than the time between subsequent atom arrivals at the island, it can be seen that the probability for two adatoms to be on the island simultaneously increases if the mean residence time of the first adatom increases and if the time between subsequent adatom arrivals decreases. Finally, by multiplying the result with the number of atoms deposited on the island per unit time $(\Delta t)^{-1}$,

$$
\omega = \frac{\tau}{(\Delta t)^2}
$$
Thus, the nucleation rate on the island for \( \tau \ll \Delta t \) in the strong barrier regime is obtained by

\[
\omega = \frac{\pi^2 F^2 R^5}{2\alpha \nu'}
\]  

(2.12)

What we can see is that the nucleation rate decreases with increasing intralayer hopping rates \( \nu' \) and distances \( a \) between NN, and increases with deposition rate \( F \) and the radius \( R \) of the island. For strong barriers, a lonely adatom may diffuse around on the island multiple times, but eventually leave after a mean time \( \tau \). Subsequently, since \( \tau \ll \Delta t \), deposition of another adatom will not take place for a relatively long time, and the island remains empty for a mean time interval \( \Delta t - \tau \). It does not sound intuitive that two adatoms could ever find each other if the first one diffuses off the island before the second one arrives. This could be explained by that the island has to grow large enough so that \( \tau \) becomes comparable to \( \Delta t \), but nucleation takes place much earlier before the island has grown to such a size. This is because of large fluctuations in the distributions of the time intervals \( \tau \) and \( \Delta t \), so for times \( \Delta t \) shorter than the mean, and for times \( \tau \) longer than the mean, i.e. for especially short times between subsequent adatom arrivals to the island and for especially long residence times for the first adatom, a second adatom may arrive to the island before the first one has diffused away, and they may meet and nucleate. Thus, top-layer nucleation is induced by large fluctuations of the adatom density caused by the random nature of the deposition process. For weak and medium ES barriers, however, the probability for two adatoms to encounter each other on an island layer decreases, since it becomes easier for adatoms to diffuse off the island, as reflected in a high value of \( \nu' \).

### 2.5 Island growth on weakly interacting substrates

A thermodynamic system always strives to minimize its free energy. Hence from a thermodynamic point of view, the formation of 3D islands is the result of the minimization of the surface free energy between the thin film and the substrate, as seen in the Volmer-Weber free energy equation

\[
\gamma_S < \gamma_D + \gamma_{\text{int}}
\]  

(2.13)

where \( \gamma_S \), \( \gamma_D \) and \( \gamma_{\text{int}} \) are the surface free energies of the substrate, the deposit and the interface between the substrate and the deposit, respectively, since the system will then strive to reduce the area of the substrate that is covered by metal deposit [11] [12]. This takes place when the bond strength between deposit atoms is stronger than the bond strength between deposit and substrate atoms [13].

Epitaxial thin film theory cannot be directly applied for amorphous weakly interacting substrates (\( SiO_2 \), glass for example), since the grains that they consist of are randomly oriented in the substrate, adsorption sites are randomly spread over the surface and therefore there is no long-range periodicity in the substrate.
Figure 2.7: a) An illustration of upwards transport to the first layer of a metal island on a WIS, b) shows the assisted upstepping mechanism for the atom at position $x_c$, c) illustrates the energy landscape along the side facets of a 3D island. Picture from [11].
KMC simulations has shown that the formation of Ag 3D islands take place already at coverages of $5.0 \cdot 10^{-4}$ ML for a growth temperature of 350 K [11]. Here, the first layer of the islands only contains seven atoms, and they are therefore not likely to capture adatoms directly from deposition, which indicates that second layer nucleation is driven by the ascent of adatoms from the substrate to the top of the island. The only efficient way for the islands to increase their heights is by trapping adatoms on their top layers. Simulations has also shown that for thin film growth of Ag on weakly-interacting substrates, the islands that form have a three-sided pyramid shape with side facets.

While it is probable in a homoepitaxial situation for an adatom to be bound at the kink or even the edge of the lowest layer of an island—since the coordination numbers are high there—for WIS it is instead more probable that the metal adatom diffuses to the top of the island since the metal atoms are more strongly bound to each other than to the substrate atoms, facilitating 3D growth, see figure 2.7 a). However, a weak bond between the adatoms and the substrate can only influence the initial growth stages of the 3D islands. A phenomenon known as assisted up-stepping may help to explain the ascent of adatoms in the early stages of growth. This assumes a reduction in the energy barrier for an atom ascending to an upper layer. This means that if an edge adatom is in a position with horizontal proximity to other atomic steps (lower and higher), it may encounter a lower energy barrier for stepping up to the higher layer, see figure 2.7 b).

It has been shown that there exists an atomistic pathway which allows for transport of atoms from the lower to the upper layers of metal islands on WIS [11]. Facile substrate detachment leads to a fast expansion of the upper layers until their edges reach those of the layers underneath, creating a smooth sidewall facet between the substrate and the island top. The growth of the side facets is promoted by low residence times of the adatoms on the sidewalls, and a low rate of adatom generation from kinks along the periphery of the facet. The formation of side facets rather than a structure with steps allows the adatoms to diffuse upwards while encountering a low diffusion barrier (compared to the step-edge barrier) on their way to the top, and this allows for an efficient interlayer transport process, see figure 2.7 c). The limiting process for vertical growth has been found to be the rate at which adatoms cross from the side facets to the top [11]. An increase of temperature enhances inter-layer diffusion processes, which in
turn leads to a more pronounced 3D growth. It has been shown that the 3D islands evolve in a self-similar manner, i.e. after enough surface coverage the aspect ratio $h/r$ between the island height and base radius saturates and reaches a steady state value.

The second layer nucleation theory can not be directly applied to explain metal growth on WIS since the starting assumption is that the island top only captures adatoms directly via deposition, and does not take into account adatom capture by upwards diffusion from lower layers. This implies that the rate of atoms arriving to the top layer is larger than what the second layer nucleation theory states, and thus the assumption that $\tau \ll \Delta t$ does not hold, since $\Delta t$ only takes the deposition rate into account.

The hypothesis made in this thesis is that the nucleation probability on top of islands is negligible until the top reaches a certain critical size, and then the probability increases fast. In this way, the side facets must grow until the top facet is large enough to host nucleation of new top layers, until the top becomes too small again and nucleation of new side facets must take place. This repeated cycle of facet-formation and height growth was investigated using KMC simulations.

2.6 The kinetic Monte Carlo method

Monte Carlo is an umbrella term for a wide sort of stochastic algorithms that use random numbers to solve problems [16]. It is named after the famous casino at Monte Carlo in Monaco and refers to the random nature of gambling. The kinetic Monte Carlo algorithm (KMC) was developed in the 1960's, although it wasn’t commonly known as kinetic Monte Carlo until the 1990s’ [16]. KMC is a stochastic algorithm that evolves a system dynamically from one state to another and it has been applied for studying diverse problems, for instance modeling the stock market, the behaviour of galaxies and thin film growth [1] [4] [17]. KMC simulations are useful for studying the time evolution of systems with many particles over long time scales (typically in the range of seconds) compared to those that can be reached with molecular dynamics (MD) simulations [6] [16]. MD is a deterministic approach which solve Newton's equations of motion for a many-body system for each time step [1] [12] [14]. One has to provide an accurate interaction potential between atoms [1], and then let the system unfold, while for KMC the user has to know what processes can occur in the system beforehand so that the system can be modelled accurately. An important limitation of MD is that the time steps need to be sufficiently short, typically about $10^{-13}$ s to $10^{-15}$ s for the atomic vibrations to be simulated with enough accuracy [14]. A disadvantage is that this puts a limit on the total simulation time that is possible to achieve, which is typically less than a microsecond, which is too short to follow atomic processes such as diffusion across a surface which takes place on much longer time scales. Since surface diffusion is essentially a random process and the KMC algorithm can simulate systems containing more atoms on much longer timescales, KMC is well suited for investigating thin film growth and comparing results with experimental data.

A state is an energetically favourable configuration of a system, which corresponds to a minimum in the associated energy landscape. This energy minimum is known as a basin. Between every pair of states, there is an energy barrier that the system has to overcome in order to make a transition to another state, see figure 2.9. After each transition the entire system is
considered to evolve to a new configuration. A system vibrates inside the basins as an effect of its thermal energy, but as long as it remains in a certain basin it does not change its state. If the system spends a long time in a basin compared to the time of a vibrational period, it is an infrequent-event system. A property that follows from an infrequent-event system is that it does not keep memory of how it reached its current state, i.e. the probability that the system moves from a state $i$ to another state $j$ is not dependent on which state the system was in before state $i$. Therefore the system has the same probability at each instant to find an escape path to another system as it had in the previous time step. A system in a state $i$ moves to another state $j$ through a set of pathways with corresponding rate constants $k_{ij}$ which are directly proportional to the transition probabilities [16]. A rate constant $k_{ij}$ is the probability per unit time that the system escapes from a state $i$, to another state $j$. The shapes of the potential basins $i$ and $j$ as well as the saddle point connecting basin $i$ and $j$ influence the rate constants $k_{ij}$. The definition of the rates $k_{ij}$ requires the associated processes of the system to be infrequent, which is the fundamental assumption needed to apply the KMC algorithm. If all of the rates are calculated correctly for every move from one state to another, then the trajectory through states that the system takes will be indistinguishable from that of an MD simulation, i.e. the overall macroscopic evolution of the system will be the same for an MD as for a KMC simulation [16]. The rates associated with each possible event are calculated using transition state theory (TST), which is a good approximation for solid-state diffusive events [16]. The output from a TST calculation is the rate constant for crossing from a state A to another state B, when atomic vibrations are neglected [14] [6]. Harmonic TST (HTST) is a further harmonic approximation of TST, and is often used to calculate rate constants for KMC simulation as well.

The transition probability between two states $i$ and $j$ is $1 - p_{\text{survival}}$, where $p_{\text{survival}}$ is the probability that the system remains in a state $i$.

$$p_{\text{survival}}(t) = \exp(-k_{\text{tot}}t)$$  \hspace{1cm} (2.14)

Here $k_{\text{tot}} = \sum_j k_{ij}$ is the sum of all rates in the state $i$, i.e. the total escape rate for escaping the state [16]. The probability distribution function $p(t)$ for the time of first escape from the

Figure 2.9: An illustration of a simple energy landscape with two states $i$ and $j$. An energy that is in a state $i$ has to overcome an energy barrier between $i$ and $j$ in order to transition to state $j$. 
state can be obtained by first integrating equation 2.14 to a time $t'$, to obtain the probability that the system has stayed in that state until time $t'$. Then the probability $p(t)$ that the system has escaped from the state must be equal to $1 - p_{\text{survival}}(t')$.

$$\int_0^{t'} p(t)dt = 1 - p_{\text{survival}}(t')$$

$$\Rightarrow p(t) = \frac{d}{dt'}(1 - p_{\text{survival}}(t')) \Rightarrow p(t) = \frac{d}{dt'}(1 - e^{-k_{\text{tot}}t'}) = k_{\text{tot}}e^{-k_{\text{tot}}t'}$$

The average time $\tau$ for escape is the mean of the distribution,

$$\tau = \int_0^\infty tp(t)dt = \frac{1}{k_{\text{tot}}}$$

There is also a corresponding probability for escape along each pathway, i.e. for each rate constant calculated for the current state, $p_{ij}(t) = k_{ij}e^{-k_{ij}t}$.

The length of the time step that the simulation should be moved forward after undergoing a certain process is found by drawing a random number from the exponential distribution,

$$t_{\text{draw}} = -(1/k_{\text{tot}})\ln(r)$$

(2.15)

where $r$ is a random number between 0 and 1. Note that the time that the system is advanced does not depend on the rate of the particular event chosen, but on the sum of all rates at the current state. The random numbers generated are pseudo-random numbers, generated in a deterministic way from a starting seed that has to be provided [6]. This seed has to be unique in order to make sure that a simulation does not evolve in the same way as another simulation.

The input that a regular KMC algorithm needs is a catalog of possible events that can occur in the system, such as diffusion jumps of atoms, or possible chemical reactions in a solution [6]. An incomplete or faulty process catalog leads to a non-physical evolution of the associated system. If more than one event can take place at a certain time, the probability for a certain event to take place is proportional to its rate relative to the rate of every other event in the catalog. At the beginning of each KMC time step, see figure 2.10, a list is created with all possible processes that can occur in the system where the size of each entry is scaled according to its probability to occur like in figure 2.11 [6]. Then a random number $r$ between 0 and 1 is generated and used to choose a random event along the stack of objects. Then a time step is chosen from the exponential distribution shown in equation 2.15, the system performs this event, advances the time and updates the list of processes and rates in the next time step since the system will be in a new state, and repeats this cycle [14]. In this way events are chosen according to their probability to occur, and an event is always chosen in each time step.

The way that a process is chosen in code is by multiplying $r$ with the total length of the rate list, $k_{\text{tot}}$. Then an array of partial sums is created, which is a sum of all rate constants up to and including rate constant $j$,.
Figure 2.10: Flow chart of the basic structure of a KMC time step.

Figure 2.11: An illustration of the process list used in the KMC algorithm. A random number $r$ is used to point to a process in the list, if $r = 0$ it points to the beginning of the list, if $r = 1$ it points to the end. The space that a process occupy in the list correspond to its rates, and thus its probability to occur. Therefore, processes with higher rates occupy more space in the list and are more likely to be chosen by the random number.
Then the first element that satisfies \( s(j) > r \cdot k_{\text{tot}} \) is chosen as the pathway that the system will follow, see figure 2.12. This is the "n-fold way" algorithm, which was first described in a paper from 1975 by Bortz, Kalos and Lebowitz [2]. This rejection-free algorithm chooses an event at every time step, which then occurs, thus avoiding simulating the time that the system spends in potential wells, only including the jumps between states [6].

There are some problems that may occur during a KMC simulation, such as what is known as the low-barrier problem, in which the processes corresponding to low barriers may be too easy to choose at each time step, causing the total available simulation time to decrease [16]. Related to this problem is the probability of a system entering a superbasin, which is a subset of basins with low energies, where it may get stuck and only transition between this subset of states. A solution is to raise the lowest barriers to slow down the fastest rates, which may increase the total time that the KMC simulations can reach, but which consequently may introduce flawed dynamics.

An important limitation of a regular KMC method is that all possible events that can occur in the system have to be known beforehand so that they can be provided as input for the simulation. Pathways that are out of our knowledge can thus not be included, until they are observed. Exchange diffusion, for example, was not discovered as being the primary diffusion pathway on Al(100) until 1990 [16]. KMC simulations of Pt on Pt(100) that neglects exchange diffusion gives a flawed description of the diffusion dynamics. In addition, including more complicated processes in the KMC rate catalog may be difficult even when they are known. A possible solution to this problem is a variant of KMC, known as self-learning kinetic Monte Carlo.
Carlo, in which the rate catalog is updated *ad hoc* for each state that the system reaches. This variant of KMC explores the local environments to find the possible transition pathways and calculates their associated rates, then these rates are stored [16].

In the context of thin film growth, a state is defined as a certain atomic configuration for the system in which the net force acting on every atom is zero [16]. The physical interpretation of the system transitioning between two states in this context is that all of the atoms in the system vibrate around their equilibrium positions, which generates vibrational energy that may give an adatom enough energy to make a jump to another lattice site. When an atom moves, the entire system is taken to a new state as the consequence of the atom changing its position. For a diffusion problem a catalog of all possible jumps for an atom has to be created, e.g. diffusion over a surface, over a ledge, across A- and B-steps, etc. depending on the code [6].

In a KMC simulation the atoms of a system are usually mapped onto a lattice with discrete positions. This is a simplification, since in reality the atoms may not be positioned exactly on their lattice points due to being close to a defect, but if each atom is much closer to a certain lattice point than to any other lattice point it is safe to map the atoms onto a lattice to simplify the implementation of the KMC algorithm.

An atom that has performed a jump from one site to another does so in a *local environment* which is comprised of its neighboring atoms, see figure 2.13. The local environment of an atom is used to calculate the rate for a jump, and by increasing the size of the local environment, the rates will be more exact, at the expense of an increase in the processing time, since more atoms have to be considered. By only updating the processes of the atoms in the local environment of an adatom that has moved during a KMC time step, instead of updating the processes for every atom in the system, computational time is saved. In this way, the rates of atoms that are not affected by the jump are saved, and they do not have to be recalculated at the next time step [16]. In figure 2.13, only the processes of the atoms that are included in the local environment of the moving adatom are updated.

A widely used procedure to compute the rates for diffusive jumps is by calculating their associated energy barriers by additive interactions, i.e. by taking the amount of neighbors and their binding energies into account for a certain adatom at its initial position and at its saddle points:

\[
E_{\text{static}} = E_{\text{sad}} - E_{\text{min}}
\]  

(2.17)

\(E_{\text{static}}\) is the energy barrier that an atom has to surmount in order to move from its initial position to another one, see figure 2.13. \(E_{\text{sad}}\) and \(E_{\text{min}}\) are the energies that the atom has at the *saddle point* and at its initial position. These energies are functions of the amount of neighbors and their binding energies to the adatom, to determine how strongly bound the adatom is at each point.

It is important to note that the process list is provided in different ways for different types of KMC codes. In some codes the entire process list containing the activation barrier of every possible transition that the system can make has to be provided beforehand, whereas in self-learning KMC, the process list is instead created at the beginning of every time step. What is common among these variants is that the local environment is scanned so that a corresponding
Figure 2.13: Illustrations of an atom jumping to a vacancy, with corresponding energy diagrams. The shaded atoms are the local environment for the atom. a) is before the jump, b) is at the saddle point, and c) is at the new position.

The process can be selected from a provided list or calculated on-the-fly.
Simulation methodology

3.1 KMC algorithm

The problem was approached using UniKMC, a simulation code developed in C++ in the Nanoscale Engineering Division at Linköping University, which implements the KMC algorithm in order to simulate thin film growth by physical vapor deposition on a hexagonal surface [11]. UniKMC is parametrized to simulate growth of Ag, but can be extended to simulate other metals. The software implements a fully atomistic model, and therefore macroscopic parameters such as a critical island size $i^*$ do not have to be provided, but what has to be provided are the atomic parameters, i.e., the interatomic bond energies. The processes implemented in UniKMC are adatom deposition and diffusion. Two sublattices, an FCC and an HCP sublattice are implemented and periodic boundary conditions (PBC) are established in the directions perpendicular to the growth direction of the film, hence atoms in one side of the simulation box will interact with atoms in the other side of the simulation box, see figure 3.1. A process list does not have to be provided beforehand, since processes are identified and created ad hoc for each new state that the system enters.

The activation barriers for adatoms to transition between two adjoining sites are calculated via a bond counting scheme (BCS), which is based on a model developed by Michely et al. for Pt/Pt(111) [12], where only nearest neighbor interactions are considered. In the BCS the activation barrier $E_{Act}$ is obtained by summing three independent energy terms

$$E_{Act} = E_{Kin} + E_{Bond} + C_{Step}$$  \hspace{1cm} (3.1)

where $E_{Kin}$ is the kinetic energy barrier, $E_{Bond}$ the difference in potential energy between the initial and final sites of the process, and $C_{Step}$ is an energy term which accounts for the ES-barrier when the adatom crosses a step. These energy terms are calculated as a function of nearest neighbors (NN), next nearest neighbors (NNN) and interatomic bond energies. The local environment is limited to NN and NNN in UniKMC, since atomic positions further away would not improve the accuracy of the simulations significantly, but instead increase the computation time exponentially. For larger coordination numbers at the initial with respect to the
Figure 3.1: An illustration of the periodic boundary conditions. The simulation box in the middle square is repeated in all in-plane directions, so that atom 1 can be considered to interact with atom 2 and atom 4, since they are within a certain interaction radius of atom 1 in their respective copies of the simulation box.

At every KMC time step in UniKMC, the following events take place (figure 2.15). First, a list of rates associated with deposition and all possible diffusion jumps on the surface is created. Then, a process is randomly chosen from the process list. This leads to the move of an atom, or the deposition of a new atom. The system is then moved forward in time by \( t = \frac{1}{\sum \Gamma_i + F} \), where \( F \) is the deposition rate in ML/s and \( \sum \Gamma_i \) is the sum of all rates. The local environment of the chosen process is then updated. Only processes that are related to atoms in the local environment of the chosen process are updated, and the rest of the processes are not, since their own local environments remain unchanged.

The atomic positions of the hexagonal lattice are labelled using a non-orthogonal coordinate system \((x', y', z')\) which is related to the cartesian system \((x, y, z)\) by the following coordinate transformation (see figure 3.2),

final site, the activation barrier is larger, since the atom moves to a less stable position. The activation barrier \( E_{Act} \) is used for calculating the rates, by using the Arrhenius equation (eq. 2.1), using the prefactor \( \nu_0 = 1.25 \cdot 10^{13} \text{Hz} \). This value was obtained by calculating an average over published experimental and theoretical values for \( \nu_0 \) [11]. Weakly-interacting substrates are implemented by lowering the pairwise bond strength between adatoms and substrate atoms \( E_{B,sub} \) with respect to the pairwise bond strength between adatoms \( E_{B,film} \). This results in a reduced activation barrier for adatoms to ascend from the substrate onto the second layer of the islands and sidewall facets.
Figure 3.2: Illustration of the cartesian and the tilted coordinate system. The blue circles correspond to atomic positions in the fcc lattice.

\[
\begin{align*}
  x &= x' - \frac{1}{2}y' + \frac{\alpha}{2} \\
  y &= \frac{\sqrt{3}}{2}y' + \frac{z'}{\sqrt{3}} - \frac{\alpha}{2\sqrt{3}} \\
  z &= \sqrt{\frac{2}{3}}z'
\end{align*}
\]

where \(\alpha\) is a parameter which takes the value 0 for fcc and 1 for hcp positions. \((x', y', z')\) take integer values.

Each simulation must be provided with a unique random seed for the sequence of numbers generated to be unique. Thus, for two equal systems simulated at the same deposition conditions with the random seed being the only parameter that differs, the chosen processes will not be exactly the same for each one, i.e. new adatoms may be deposited in different positions for each simulation, different adatoms may be chosen to move, and the chosen adatoms may move to different positions. However, the simulations will evolve macroscopically in a similar way.

The morphological evolution of the simulated system is visualized using the free software package Ovito [15].

### 3.2 Island shape quantification

In order to understand how the growth morphology of metal islands on weakly interacting substrates depends on the temperature \(T\) and the bond strength with the substrate a grid (3D color map which represents the height-to-base-radius aspect ratio of islands simulated at different temperatures and binding energies) was refined i.e. simulations were performed with
narrower increments in temperature and binding energies than what had been done before in order to obtain a grid with higher resolution. In order to generate the refined grid, a set of simulations of single island growth on weakly interacting substrates were performed for the T range between 250 K to 500 K in increments of 25 K, and for $E_{B,sub}$ ranging between 50\% to 75\% of $E_{B,film}$, in increments of 2.5\%. F was set to 10 ML/s and the aspect ratio was extracted when the coverage reached 0.5 ML. Hcp sites were removed from the substrate in order to simulate an amorphous substrate. All simulations were carried out in a simulation box with a size of 100x100 atoms. The aspect ratio was defined as $h/R$ where the height $h$ is the total height of the island and the radius $R$ is the radius of a circle with an area equivalent to the base area of the island.

The geometrical parameters of the islands were calculated with regards to the tilted coordinate system, as follows. We only consider fcc positions since hcp sites are unstable in the simulations. The lattice constant for Ag is 4.079 Å, so that the distance $a$ between NN in the fcc structure is $a = \frac{4.079}{\sqrt{2}}$ Å. $a$ is used to scale the units in the cartesian coordinate system to Å. The area occupied per lattice point could be calculated as the area of a parallelogram formed by the distance $b$ between atoms in the x direction, and the distance $h$ between atoms in the y direction, see figure 3.3, so that

\[ b = a \]
\[ h = \frac{\sqrt{3}}{2}a \]

\[ \text{Area} = b \cdot h = \frac{\sqrt{3}}{2}a^2 \]
hence the total area of a layer is

\[ A = \frac{\sqrt{3}}{2} a^2 \cdot N \]

where \( N \) is the number of atoms in the layer. From this, the radius of a layer was calculated as the radius of a circle with an equivalent area \( A \), as

\[ R = \sqrt{\frac{A}{\pi}} = \sqrt{\frac{N}{2\pi}} \sqrt[4]{3} a \]

The height of an island is

\[ h = z \cdot \sqrt{\frac{2}{3}} a \]

where \( z \) is the number of layers that the island consists of. Scripts were written using Bash Script in order to calculate the final aspect ratios of all the simulated islands, and to create a data file consisting of all the aspect ratio ratios for each temperature and binding energy, to make plotting a graph convenient. MatLAB software was used for generating the graphs.

### 3.3 Determination of critical radius

The critical radius \( R_c \) of a top layer \( L_1 \) is defined as the radius that layer had at the moment a successful nucleation event occurred on its top. A nucleation attempt is assumed to be successful only when the new layer does not dissociate, which implies that the new layer \( L_2 \) must grow until it reaches a sufficient large size to host another nucleation event on its top (figure 3.4). The dissociation probability of the new layer \( L_2 \) is then assumed to be negligible.

Since there is no strict definition for what constitutes a nucleation event in the literature, for the purpose of this thesis, two atoms are considered to have nucleated when the distance between them is equal to or smaller than 3.33 Å, i.e. as when two atoms are in neighboring fcc sites, neighboring hcp sites or as when one atom is in an fcc site and the other in a neighboring hcp site.

A subroutine was implemented in UniKMC for calculating \( R_c \) and the number of nucleation attempts on each layer as a function of the coverage that had been reached at the moment that layer hosted a successful nucleation event. The subroutine begins to run at every KMC time step when the island consists of at least three layers. See figure 3.4 for illustrations and figure 3.5 for a basic flow chart of what the subroutine does at every KMC time step. For detailed flow charts, see Appendix A. At the beginning of every KMC time step the subroutine checks if nucleation of a layer \( L_2 \) has occurred on a layer \( L_1 \). If it has, and this is a new nucleation event, the subroutine counts up the number of nucleation attempts on this layer and saves the radius of \( L_1 \) as the possible value of \( R_c \) for the layer. Then the subroutine checks if a nucleation event has occurred on top of the layer \( L_2 \), if it exists. If it has, the radius that \( L_1 \) had when
Figure 3.4: An illustration of what the subroutine calculates. In a) two adatoms are present on the layer $L_1$. In b) a nucleation event has occurred on top of $L_1$. In c) the new layer $L_2$ has grown enough so that a nucleation event has taken place on top of the new layer. From this time, the probability of dissociation of $L_2$ is negligible. The nucleation event of $L_2$ in (b) is deemed as successful, if $L_2$ did not dissolve between (b) and (c).
the nucleation of the first two atoms of layer $L_2$ occurred is the $R_c$ for this layer, thus $R_c$ and the coverage of that moment is saved for this layer. Then the subroutine moves up a layer and begins to check if a successful nucleation attempt has occurred on top of the layer $L_2$, which is now redefined as the layer $L_1$ and the subroutine does the same procedure for every layer of the island.

The subroutine works both for simulations starting from deposition on an empty substrate and from an already existing island. When a simulation is continued, the subroutine identifies the two highest layers on the island and defines them as $L_1$ and $L_2$. When loading a simulation the possible $R_c$ that a layer may have been assigned in the previous simulation run is not considered. This may lead to an overestimation in the value of the first $R_c$ that is calculated in each loaded simulation, since the layer $L_1$ may have grown since its possible $R_c$ was identified in the previous simulation run. If several different values of $R_c$ for the same layer is found in the result files, it is the first calculated value that is correct if it associated to more than one nucleation attempt, and all values that come after can be neglected. The error due to loading the simulations is small (5-10 atoms) at high temperatures since the layer formation is fast, but can not be neglected for simulations run at 300 K where the formation of new layers is slower and the error may be as large as 70-80 atoms. Thus, for simulations carried out at 300 K for layers where the subroutine calculated only 1 nucleation attempt the calculated $R_c$ can be considered to be false, and is not included when calculating the average value of $R_c$.

The output from the subroutine was compared with visualizations of the simulations [15]. For every nucleation attempt and nucleus dissociation event on top of a layer, visualization was printed out at the same time in order to confirm that the $R_c$ calculated by the subroutine was correct, i.e. that it was measured from a point in time when a successful nucleation attempt of
L₂ had taken place, and so that the subroutine detected each nucleation attempt and nucleus dissociation according to their definitions.

In addition, to ensure that the number of nucleation attempts that the subroutine calculates is physically possible, the activation barriers for dissociation of a dimer, for when one of the atoms performed an fcc→fcc jump or an fcc→hcp jump were calculated and used in the Arrhenius equation (equation 2.1). The activation barriers were calculated using the formalism of the BCS implemented in UniKMC.

3.4 Simulation strategy

The parameter space with respect to growth temperature and adatom/substrate pairwise bond strength was scanned in order to identify the 3D growth regime, so that a certain set of values of deposition conditions was selected for which 3D growth can be observed. Simulations at temperatures ranging from 300 K to 500 K in increments of 25 K, with a deposition rate of 10 ML/s were carried out with the subroutine, until a coverage of 1 ML was reached for every simulation. The binding energy between Ag atoms and substrate atoms was set to be 50% of the binding energy between two Ag atoms.

5 independent simulations with different random seeds were performed at each temperature in order to calculate statistics for Rₖ, using the mean and estimating the error with the standard deviation, see Appendix B for more details. The average value of the critical radius for each simulation was calculated from a point in time when the aspect ratio (h/R) had reached a steady-state value, because from that point in time the value of R oscillates around a constant value.
• Chapter 4

Results and discussion

4.1 Island shape evolution

The refined grid which plots the steady-state values of the aspect ratios, \(h/r\)\(_{SS}\), at 0.5 ML as a function of T and \(E_{B,sub}/E_{B,film}\), aided in deciding at which temperatures and at which value of \(E_{B,sub}\) simulations using the subroutine should be carried out for, since the project goal is to investigate the morphology of 3D islands.

In the refined grid, figure 4.1, two distinct regions can be observed, with a narrow transition zone in between. The top-left quadrant corresponds to \(h/r\)\(_{SS}\) = 1.85, and thus to pronounced 3D morphologies where the islands consist of many layers, while the bottom-right quadrant corresponds to \(h/r\)\(_{SS}\) ranging from 0.03 to 0.6 and thus to pronounced 2D morphologies where the islands are rather flat and consist of few layers. For \(E_{B,sub}/E_{B,film}\) > 0.7 the islands exhibit 2D morphologies for all simulated temperatures. With decreasing values of \(E_{B,sub}\), the lowest temperature required in order to observe 3D growth decreases as well. For \(E_{B,sub} = 0.5E_{B,film}\) the range for T where 3D morphologies can be observed is the largest, thus simulations using the subroutine were performed at this value of \(E_{B,sub}\).

4.2 Critical radius evolution

The behaviour of the aspect ratio and \(R_c\) as a function of coverage for 300 K, 400 K and 500 K is shown in figures 4.2 - 4.4. At the initial forming stages of each island the aspect ratio increases rapidly, until it reaches a steady-state value which is reached faster at lower temperatures. Each rapid increase of the aspect ratio indicates that a new layer is formed, and at each slow decrease the height is constant and the radius increases. The average size of \(R_c\) is larger and the range of the values is wider at 300 K (5 - 16 Å), than at 500 K (5.2-7 Å). \(R_c\) steadily increases at 300 K. At 400 K and 500 K, \(R_c\) oscillates around a steady-state value beyond the early stages of growth. At 300 K from 0.05 ML to 0.2 ML, \(R_c\) and \(h/R\) increases rapidly. Figures 4.3 - 4.4 suggest that new layers form relatively fast during the early growth stages at higher temperatures, where the sharpest increase of the aspect ratio can be observed.
and where $R_c$ fluctuates more, because the islands are then still small, and it takes a relatively short time for new side facets to form and increase the width of the island top.

The results show that the average size that an island top needs to reach before successful nucleation of new, stable layers can take place decreases from 300 K to 375 K, until it reaches a steady-state value from 375 K to 500 K (figure 4.5). Between 300 K and 375 K the average $R_c$ decreases from 17.5 Å to 6 Å, and from 375 K to 500 K it reaches a steady-state value of 6 Å. The error bars are wider for low temperatures, which indicates that the values of $R_c$ fluctuates more at low temperatures than at high temperatures, especially at 300 K, since 300 K lies in the transition region between 2D and 3D growth, and the simulations yield qualitatively different morphologies for different random seeds at this temperature. The decrease of the average $R_c$ for temperatures up to 375 K indicates that the 3D growth becomes more pronounced, and the steady-state value of the average $R_c$ indicates that the 3D growth does not become more pronounced for temperatures higher than 375 K, which agrees with the aspect ratios that can be observed in the refined grid, see figure 4.1. This suggests that the top layers have reached the average minimum size at which they can host successful nucleation events for $T \geq 375$ K. Thus, for smaller top layer sizes many nucleation attempts may take place, but the probability for the nucleus to expand and become stable is low.

Geometrically, a nucleation event may occur on top of a layer as small as 5 atoms. 10 atoms is the smallest size that a layer needs to have in order to host a layer consisting of 5 atoms, see figure 4.7. However, this requires that the second layer is stable a sufficiently long time and that the rate of adatom arrival to the top is sufficiently large for two adatoms to meet and nucleate. For growth at high temperatures of metal islands grown on WIS, the smallest
Figure 4.2: $R_c$ and aspect ratio as a function of coverage at 300 K.

Figure 4.3: $R_c$ and aspect ratio as a function of coverage at 400 K.
Figure 4.4: $R_c$ and aspect ratio as a function of coverage at 500 K.

Figure 4.5: The average $R_c$ as a function of temperature.
Figure 4.6: Snapshot of a simulation at 450 K.

Figure 4.7: Illustration of the geometrically smallest layer size for hosting a successful nucleation event. The white circles are possible sites on the top layer where adatoms can reside.

value of $R_c$ that can be observed for higher layers is $R_c = 5.2$ Å, or 12 atoms (fig 4.4). The steady-state value of the average values of $R_c$ for $T \geq 375K$ is 6-6.5 Å (or about 15-19 atoms). These higher average values may be explained by the small coordination numbers of all atoms that are close to the edge of the top, since they may detach and diffuse down to the side facets more easily at higher temperatures since they are then more mobile. Higher temperatures also increase the instability of the layers, as indicated by figures 4.8 and 4.9, since the number of nucleation attempts required before a new layer successfully forms increases.

The average number of nucleation attempts for each layer is higher at 500 K than at 300 K (figures 4.8 - 4.9), it peaks at 500 K during the formation of the first layers, and then decreases. At 300 K the number of nucleation attempts reaches a peak before 0.5 ML. A weak correlation between $R_c$ and the number of nucleation attempts can be seen, in that when the slope of the $R_c$ is positive, the slope of the number of nucleation attempts is often positive as well. As indicated by the number of nucleation attempts seen in figures 4.8 and 4.9, it seems more probable for a layer to dissolve at 500 K than at 300 K, i.e. layers are on average more stable at 300 K. This can be explained by the increased number of processes that take place on the island tops at higher temperatures during the island evolution. The processes that influence the adatom density on the top layer are the deposition of adatoms directly onto the top layer, upwards diffusion along the side facets to the island top and downwards diffusion from the top to the side facets. Direct capture of deposited adatoms on the island top is highly unlikely due to the relatively small surface area of the top layer compared to the area of the substrate, and can thus be neglected as an influencing process. Therefore it is upwards diffusion of substrate and side facet adatoms that is the main source of adatoms to the top layer.

The increasing number of nucleation attempts for higher temperatures may be explained by the
Figure 4.8: The number of nucleation attempts and the $R_c$ as a function of coverage at 300 K.

Figure 4.9: The number of nucleation attempts and the $R_c$ as a function of coverage at 500 K.
fact that at higher temperatures clusters are more likely to dissociate since the atoms may have sufficient kinetic energy to break their lateral bonds and then diffuse from the top layer. The transport of adatoms to higher layers along the side facets is increased at higher temperatures as well. Since the 3D growth continues at high temperatures, the upwards transport of adatoms occurs at a high enough rate so that it is possible for two adatoms to be present on the top layer simultaneously in order for a nucleation event to occur. Since cluster dissociation is more likely at high temperatures, an adatom that reaches the top layer from a side facet is more likely to encounter a lonely adatom on the top than it is to counter a cluster. Conversely, for lower temperatures the number of nucleation attempts is lower since the kinetic energies of the adatoms are lower and upwards transport along the side facets is not as efficient. The clusters are also less likely to dissolve, i.e. they are more stable, so that it is more likely for an adatom that reaches the top that there is already a stable cluster into which it can be incorporated, i.e. an adatom that reaches the top layer at lower temperatures is less likely to participate in a new nucleation attempt.

What is observed on higher layers for metals on WIS, is that the number of nucleation attempts increase with increasing temperatures and thus for increased interlayer transport. As seen in the equation for nucleation rate on the second layer from second layer nucleation theory, equation 2.12, as the temperature increases, the interlayer jump rate $\nu'$ increases, so that the nucleation rate $\omega$ of a second layer decreases with increasing temperatures. Therefore, second layer nucleation theory can not be directly applied for explaining the probability of nucleation on the top layers of metal islands on WIS, which can be explained by the fact that it does not take into consideration the upwards adatom transport from lower layers to the top.
Chapter 5

Conclusions and outlook

The probability for top layer nucleation on metal islands grown on weakly interacting substrates was investigated using KMC simulations. The goal was to study the way by which the radii of the top layers influence the probability of formation of a new layer, i.e. when a new layer have reached a critical radius $R_c$ so that it can host a successful nucleation event. Simulations were performed from 300 K to 500 K with $E_{B,sub} = 0.5E_{B,film}$. A subroutine was developed and implemented in UniKMC, an existing KMC software, in order to calculate $R_c$ for each layer as the islands evolve. Five simulations with different random seeds were performed at each temperature in order to gather statistics. Analysis of the simulation results show that the average $R_c$ decreases rapidly from 17.3 Å to 6 Å from 300 K to 375 K and reaches a steady state value of 6 Å from 375 K to 500 K, which suggests that the top layers have reached the minimum size at which they can host successful nucleation attempts for $T \geq 375$ K. The nucleation rate on top layers increases with increasing temperatures, thus second layer nucleation theory can not be directly applied for describing the nucleation rate on top of metal islands grown on WIS.

The development of a specific probabilistic nucleation theory for metals on weakly-interacting substrates would be a good complement to further investigate the problem that was treated in this thesis. The knowledge gathered from this project will aid in the understanding of growth of metal thin films on weakly interacting substrates, which may help to suppress the 3D growth of the islands in order to achieve smooth metal thin films.
Bibliography


A Flow charts
Figure A.1: A flow chart for the function Critical_Radius.

Figure A.2: A flow chart for the function Step_Through_XY_Plane.
Figure A.3: A flow chart for the function Set_Cluster.
Set_Layer(map -> current_island, map -> comp_island)

1. Start
2. Does current_island contain less than two atoms?
   - Yes: Return false
   - No:
     1. Does comp_island contain less than two atoms?
        - Yes: Set comp_island = current_island
        - No:
          1. Does comp_island and current_island contain the same amount of atoms?
             - Yes: It's the same island as in the previous time step. Return true
             - No:
               1. Does current_island contain one atom more or less than island_L2?
                  - Yes:
                    1. Is current_island larger than comp_island, and does it contain all of the atoms that were in comp_island in the last time step?
                       - Yes:
                         - The island has coalesced with another island
                         - Set comp_island = current_island
                         - Return true
                       - No: Return false
                    - No: Return false
                - No: Return false

Figure A.4: A flow chart for the function Set_Layer.
Figure A.5: A flow chart for the function Find_Layer.
B Statistical analysis of $R_C$ data

Statistical values were calculated for the simulations that were carried out. From statistical theory the mean $\mu_X$ and the standard deviation $\sigma_X$ of a set of values $x_i$ are defined as

$$\mu_X = \frac{1}{N} \sum_{i=1}^{N} x_i$$  \hspace{1cm} (B.1)

and

$$\sigma_X = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (x_i - \mu)^2}$$ \hspace{1cm} (B.2)

respectively, where $N$ is the total number of observations in the sample.

The central limit theorem (CLT) was used for calculating statistical properties for each set of five simulations. The CLT states that if a set of samples is collected from a population, the distribution of the mean values calculated for each sample in the set will approximate a normal (Gaussian) distribution, a common probability distribution, with the approximation getting closer to a normal distribution the more samples $n$ that are collected in each set. Furthermore, the CLT theorem states that

$$\mu_X = \mu_{\bar{X}}$$ \hspace{1cm} (B.3)

and

$$\sigma_X = \frac{\sigma_{\bar{X}}}{\sqrt{n}}$$ \hspace{1cm} (B.4)

The variable $\bar{X}$ consists of the sample mean of $X$, and $n$ is the number of values that are averaged when calculating $X$. $\sigma_{\bar{X}}$ is the standard error of $\bar{X}$. Thus, the mean of the means $\mu_{\bar{X}}$ is equal to the real mean of the distribution, and the standard deviation $\sigma_X$ decreases with increasing sample sizes.