Kinetics of nanoclusters on surfaces and in thin films

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ABSTRACT

Rapid growth of the modern microelectronics industry during recent years has called for novel methods for growth and modification of materials in the manufacturing processes. Recently nanoclusters have been considered for use in these processes. As the size of nanoclusters are in the same size range as microelectronics components, they are suitable building blocks. Developing new methods for use in the manufacturing processes require knowledge of the interaction of nanoclusters with their surroundings on the atomic level. Limitations of the experimental equipment lead to the fact that computer simulations and modelling are often the only feasible method for studying this interaction.

In this thesis our studies of the interaction of nanoclusters with their surrounding during deposition, relaxation on the surface, burrowing and irradiation with ions and electrons are reviewed. As the space and time scales of these processes span several orders of magnitude, several different computational methods have to be used. We focused on molecular dynamics (MD), kinetic Monte Carlo (MC) and the particle coalescence method (PCM).

For deposition of Cu nanoclusters on a Cu (100) surface we established a nanocluster size versus substrate temperature regime for epitaxial growth. The evolution of these nanoclusters on a long timescale was studied and the effective activation energy for this process could be determined.

The high Co island density and size distribution on Ag (100) during low energy ion deposition was studied using PCM and MD simulations. A parameter of the fragmentation kernel used in the PCM was inferred from MD simulations mimicking the conditions during low energy ion deposition.

Burrowing of Co nanoclusters into Cu (100) was studied with MD. The mechanisms of the burrowing for differently aligned nanoclusters were determined from these simulations.

Recrystallisation of amorphous nanoclusters in Si was studied with MD to which a bond-breaking model was augmented. Based on the simulation results, we determined mechanisms explaining experimental observations.
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1 INTRODUCTION

Advances in the field of microelectronics production have created an interest in faster and more reliable methods of producing high quality epitaxial as well as nanocrystalline thin films [1, 2]. Using nanoclusters as a means of achieving these goals has recently been taken into consideration [3]. Nanoclusters are interesting, e.g. for this application, due to their unusual physical properties compared to bulk solids [4]. Understanding the interaction between nanoclusters and their surroundings is crucial to the development of novel methods in this field.

The production of high quality films is important for the microelectronics industry. Both metal and semiconductor components rely on the fact that the material does not contain disturbing amounts of defects. Semiconductor components also rely on the single-crystallinity of the material. Defects can be avoided by using high quality materials and manufacturing processes and by afterwards annealing defects that have originated from the manufacturing. There is also much interest in growing nanocrystalline thin films, since these may also prove useful in the manufacturing of high density storage devices [5, 6] and other materials that require unique electronic and optical properties.

Due to the complexity of the interaction between a nanocluster and its surroundings, the involved processes can not be examined analytically. Experiments have provided valuable information on the interaction between nanoclusters and their surroundings. However, the time- and space-resolution of the experimental equipment is usually too limited to observe the kinetics, i.e. the mechanism by which a physical or chemical change is effected [7], of the processes. Atomistic-level understanding of the processes that involve nanoclusters can be gained by using computer simulations. Unfortunately no single method is suitable for this, due to the wide range of time scales, the desired measurement accuracy, and the size of the studied systems.

Molecular dynamics (MD) simulations are suitable for simulations where the time scale is limited to nanoseconds. The limitation is due to the time consuming calculations involved in the atomistic interaction calculations. Molecular dynamics has the advantage of high accuracy, assuming that the used interatomic potential model describes the interaction on the atomistic level well. Molecular dynamics simulations provide detailed information on the atomistic level, which calls for advanced analysis tools to extract the essential information.

If the time scale of the studied processes is of the order of seconds, the molecular dynamics method is clearly not suitable. Instead we used a kinetic Monte Carlo (MC) method. This method has a decreased accuracy as compared to MD but instead it has a significant increase in the magnitude of the time scales that can be simulated. In this work the Bortz-Kalos-Lebowitz MC method [8] was
chosen. It allowed us to simulate the desired systems on time scales of the magnitude of thousands of seconds and to monitor the atomistic processes.

If the point of interest is in the density of islands on a surface under certain conditions, it is easy to see that both the MD and MC methods are problematic. With both methods one faces the problem of defining islands as geometrical structures, and getting good enough statistics on the island size density distribution over the whole surface would require very long simulations. In this thesis we used the particle coalescence method (PCM) to circumvent these problems. The PCM method solves the island density and size distribution rate equation numerically by considering point-like islands of known sizes on a lattice, thus being a very efficient method for calculating the island density distribution and its evolution with time.

In this thesis I will give an overview of the numerical methods described above. Additionally I will give an overview of the interaction of nanoclusters with their surrounding matter and how this has been studied in our group using computational methods.

2 PURPOSE AND STRUCTURE OF THIS STUDY

The purpose of this thesis is to increase the understanding of the interaction of nanoclusters with their surroundings during deposition, thermal activation, and irradiation with ions and electrons.

The thesis consists of this summary and the following five articles published or accepted for publication in refereed international journals. The articles will be referred to by bold face Roman numerals in the text.

In the first paper we studied thermal deposition of Cu nanoclusters on a Cu surface. We established a cluster size versus system temperature regime for epitaxial deposition. In paper II the long time scale evolution of clusters on the surface within this epitaxial deposition regime was studied. In paper III we studied the breakup of monolayer Co nanoclusters on a Ag surface during irradiation with low-energy Co atoms. The burrowing effect of Co nanoclusters into a Cu surface and its mechanisms was studied in paper IV. In paper V we studied the mechanisms of recrystallisation of amorphous nanoclusters inside a Si thin film during electron irradiation. In papers I and IV we present novel algorithms for the analysis of the molecular dynamics simulation results.
Summaries of the original papers


In this paper a cluster size versus system temperature regime for epitaxial growth was established using thermal deposition of clusters. The studied system consisted of Cu nanoclusters which were thermally deposited onto a flat Cu (100) surface. The transformation mechanisms of a cluster in a non-epitaxial configuration to an epitaxial configuration was also presented. Two developed analysis algorithms for the analysis of epitaxiality were also presented.


Cu nanoclusters consisting of 22-2045 atoms located on a flat Cu (100) surface were studied in the temperature range 220-1020 K. The nanoclusters were observed to be reduced to a single monolayer on the surface if allowed enough time to relax. The time required for this process was simulated for all nanoclusters at all temperatures and the activation energy and prefactor could be calculated for the process. The mechanism for this process was found to have a dependence on the size of the cluster.


This work considers the breaking up of Co islands on a Ag (100) surface during irradiation of low energy (30 eV) Co atoms. Using the MD simulation results we determined the functional form of the fragmentation kernel used in the PCM simulations as well as the value of the \( \alpha \) fragmentation kernel parameter. The PCM simulations gave island size and density distributions which were identical to the experimentally observed ones. The simulations show that the experimentally observed distributions can be explained with detachment of atoms from the islands.


We present a model for the burrowing of Co nanoclusters into a Cu (100) surface. The model includes the mechanism of transformation of epitaxially landed clusters into non-epitaxial ones and the burrowing process of these. An extension to analysis algorithms for the identification of dislocations was presented in this paper. The model presented for the burrowing explains the behaviour observed in the experiments.

In this work we studied the evolution of amorphous nanoclusters inside a Si thin film during irradiation with electrons. A model for electron induced bond breaking in Si was developed. The electron induced bond breaking was found to contribute significantly to the recrystallisation as compared to other possible means. The behaviour of the recrystallisation observed in the simulations agree with the behaviour observed in experiments.

Author’s contribution

The publications presented in this thesis are the result of group work. In paper I the author developed the analysis algorithms used for simulation result analysis, run a minor part of the simulations and wrote sections I and II of the final paper. The simulations and result analysis of papers II, IV and V were performed by the author, who also wrote the majority of papers II and IV, and half of paper V. The author was responsible for the MD simulations and wrote sections I, II and IV of paper III. The author developed the extension of the dislocation analysis algorithm used in paper IV. The modifications of the potential models used in paper V were conducted by the author.

The PCM simulations included in paper III were performed by M. O. Jahma at the Helsinki University of Technology.

3 NANOCLUSTERS NEAR SURFACES

As the term indicates a nanocluster is an entity of nanometer size that consists of atoms. Since the size of a nanocluster is only a few orders of magnitude larger than that of atoms, the number of atoms in a nanocluster will be quite small, usually of the order of hundreds of thousands or less. The small number of atoms leads to the fact that most of the atoms will be at the surface or so close to it that their interaction with outside objects will not be shielded by the other atoms. This leads to a very strong interaction between a nanocluster and its surroundings, and to the fact that nanoclusters are reactive, i.e. have a high tendency to undergo change [9–12]. The structures of nanoclusters are governed by the minimum energy principle, to which the surface energies of its facets are the main contributor in the case of metal nanoclusters. Thus free nanoclusters tend to have faceted, but close to spherical shapes [13–16], while nanocluster on and in surfaces can have more complex structures due to the
interaction with the surface. The internal arrangement of atoms in a nanocluster also plays a role in the shape of the cluster as different lattice types favor different types of facets [17–19].

Reviewing experimental situations, nanoclusters are found in several different configurations. A nanocluster can for instance be either

(i) free (in vacuum)
(ii) on a surface
(iii) a monolayer on a surface
(iv) a crystalline nanocluster in a crystalline matrix
(v) a crystalline nanocluster in an amorphous matrix
(vi) an amorphous nanocluster in a crystalline matrix
(vii) an amorphous nanocluster in an amorphous matrix

In this thesis we studied case (ii) in papers I, II and IV, (iii) in paper III and (vi) in paper V.

3.1 Applications of nanoclusters

Due to the unique properties of nanoclusters, they can be used successfully in a wide variety of applications.

One of the most promising applications for nanoclusters is the growth of single-crystalline as well as nanocrystalline thin films, which have many important applications in microelectronics manufacturing. Single-crystalline films are especially interesting for use in microelectronic circuits [1, 2], while nanocrystalline materials have been found to have interesting optical, electronic, and mechanical properties [20–22]. Growth of thin films using nanocluster deposition is especially interesting because it can potentially be applied over a wider range of temperatures than molecular beam epitaxy (MBE). As shown in papers I and II, the difference between producing nanocrystalline or single-crystalline thin films is simply a matter of carefully choosing the size of the deposited nanoclusters, the temperature of the system, and the flux during deposition.

Low energy ion deposition (LEID) and ion beam assisted deposition (IBAD) can also be used to grow high-quality epitaxial films. Film growth using LEID is conducted by depositing ions (with energies in the range of 5-30 eV) onto the surface. With IBAD one thermally deposits the grown material while at the same time bombarding the surface with immiscible ions. The kinetic energy of the incoming atoms is high enough in both cases to break up islands and thus create new nucleation centers. The new nucleation centers lead to a higher island density which in turn leads to monolayer growth. Experiments with pulsed IBAD for Ag on Ag(111) and Cu on Cu(111) show that when a
pulse of energetic particles is applied in the beginning of the growth of every new monolayer, layer-by-layer growth is possible up to 7 monolayers (ML) [23]. This is believed to be due to enhanced atom detachment from the island edges, which is shown to be correct in paper III.

For the development of modern high-density storage devices it is important to efficiently manufacture materials that have a high surface density of units with highly localised magnetic moments [5]. Supported magnetic clusters on inert substrates, like noble metals or semiconductors, could potentially have these properties. These types of systems have been studied extensively with experiments [6, 24, 25] as well as with simulations [26–28]. Currently manufacturing of these materials is done by depositing layers of material and then using photolithography to separate the layers into clusters. State of the art photolithograpy methods used today have a minimum resolution in the range of 100 nm. A phenomenon discovered by Zimmerman et al. called nanocluster burrowing [29, 30], could be used to create large surface areas with a high integration of nanosized magnetic clusters. Burrowing is a process where thermally deposited nanoclusters submerge into the substrate when it is heated. Burrowed clusters have also been found to align with the substrate during the burrowing process, which was also confirmed by the simulations conducted in paper IV.

Manufacturing of modern microelectronics semiconductor circuits requires doping of semiconductor materials. This is done by ion implantation, which has the advantage of a good control of dopant depth profiles [31]. The implantation of high energy ions creates damage in the semiconductor material, which negatively affects the operation of the semiconductor. Damage in a semiconductor will usually be formed in clusters of nanometer size, which can be considered amorphous nanoclusters in a crystalline matrix. Traditionally the method of annealing this damage has been heat treatment. However, this method has the disadvantage of broadening the implant profiles which is a problem in the case of very narrow profiles [32]. The use of ion, laser and electron beams as a means for recrystallisation has previously been studied [33–36]. Recent experiments with electron beams [37] indicate that these could be used to recrystallise these amorphous nanoclusters in Si, although the mechanism for this remained unclear from the experiments. The Spaepen-Turnbull model [38] proposes that recrystallisation is due to irradiation induced dangling bonds at the amorphous-crystalline interface. According to the model these dangling bonds migrate along the interface until they form a lower energy state and thus contribute to the recrystallisation. In paper V we investigated the mechanism of this recrystallisation.
4 SIMULATION AND ANALYSIS METHODS

The investigation of processes where nanocluster are involved, range over several orders of magnitude of system size and time scale. On the other hand, the accuracy of the methods are of great importance for determining basic mechanisms of the investigated processes.

Computational methods used in physics make a tradeoff between increased accuracy and larger systems and longer time scales. Molecular dynamics can be used to investigate processes in very close detail, but the method is limited to short (≈ 1 ns) timescales. Kinetic Monte Carlo and PCM methods can be used when the focus is on the evolution of the system on longer time scales.

How to bridge these different computational methods is not obvious due to the large differences in the approach of the methods, but it is possible, as will be shown in section 4.2.

4.1 Molecular dynamics

Molecular dynamics is a computation-intensive method in which we keep track of all the atoms in the system at every instance of time. From the coordinates of the atoms the forces acting between atoms can be calculated using a predetermined potential model. When the forces are known, the Newtonian equations of motions are solved to get the coordinates for the atoms at the next instance of time. This procedure is then iteratively repeated with a certain time step until a predetermined event or time limit is reached.

In molecular dynamics simulations we can control a number of free parameters, e.g. temperature and pressure. This gives us a very efficient means of studying processes at the atomistic level under different circumstances.

Most of the scenarios simulated in papers I-V involved a free surface. In the MD simulations a free surface is implemented by using periodic boundary conditions in the simulation box in the directions perpendicular to the surface normal. In the direction of the surface normal no restrictions are set. However the bottom three atomic layers of the simulation box are fixed and a temperature scaling algorithm is applied in the following three atomic layers. Along the edges where we apply periodic boundary conditions we also apply a temperature scaling algorithm.

Temperature scaling is necessary to control the temperature, because the studied systems undergo exothermic processes, i.e. energy is released during the processes. Without temperature control the whole simulation box would heat up. In real systems the size of the system is essentially unlimited
and the heat would dissipate to the rest of the system. We apply the temperature scaling at the edges where we have periodic boundary conditions, thus creating a situation where heat dissipates out of the system at these edges. In this work we used the Berendsen temperature scaling algorithm [39]. In the simulations conducted in this work, irradiation energies are thermal or very low, therefore a more advanced method is not required.

In papers I-IV the interatomic potential was described using the embedded-atom-model (EAM) [40–46] which has been shown to describe interactions of metals [47] very well. Paper V investigates semiconductor materials, in this work we used the Stillinger-Weber potential model [48] and the Tersoff model [49] to describe interatomic interactions.

In papers I and IV the deposition of nanoclusters on surfaces was done by placing a nanocluster at a large enough distance from the surface so that no interaction between the nanocluster and surface occurred. Then the nanocluster was given a momentum in the direction of the surface. The irradiation of the substrate in papers III and V was done through a similar procedure but in those cases only a single atom was accelerated towards the surface.

For the work described in paper V the interatomic interaction model was modified. Two different models for breaking bonds were applied, the non-bond and the anti-bond model. The non-bond model implied the elimination of the attractive part of the interaction between two predetermined atoms, thus leaving the repulsive part of the potential as the only interaction. Neighbouring atoms would interact with the two atoms as described by the unmodified potential model. In the more sophisticated anti-bond model, the atoms with a broken bond would interact with a potential formed by the repulsive two-body part of the Tersoff potential model and a screened Coulomb potential [50],

\[
V(r) = \frac{1}{2} A e^{-\lambda (r + r_0)} + \frac{Z^2}{r} e^{-\alpha r}
\]

(1)

where \( A = 1.8308 \times 10^3 \) eV, \( \lambda = 2.4799 \) Å\(^{-1} \) (Ref. [49]), \( Z = 14 \) and \( \alpha = 4.0 \) Å\(^{-1} \). Two different values for \( r_0 \) have been proposed, namely 0.19 Å and 0.065 Å. The interaction of the atoms with a broken bond and their neighbours was described by a potential calculated using \textit{ab initio} simulations [51]. Transition between the normal interaction and the bond-breaking interaction models was conducted by scaling the bond breaking potential with the Fermi function, \( F(t) \), and the unmodified interaction with \( 1 - F(t) \). The interval for which the bond was broken was chosen between 5 and 250 fs. Based on experimental results [52, 53], this was considered a realistic time scale for bond reforming after excitation. To rule out recrystallisation by local heating due to the breaking of the bond, we also conducted simulations where instead of breaking the bond, the nearest atoms around the bond to be
broken were heated with the same amount of energy as the breaking of the bond would induce. This hot spot was centered on the broken bond and had a Gaussian distribution.

4.2 Kinetic Monte Carlo

As stated in section 1, molecular dynamics methods are not suitable when we wish to simulate processes on a time scale that is much larger than nanoseconds. The problem is that molecular dynamics methods apply physically realistic dynamics that lead to small, local changes of successive configurations of the system. This makes molecular dynamics inherently slow. Instead we need a method that can make those small steps at a faster pace.

If we were to use stochastic dynamics, e.g. Metropolis Monte Carlo (MMC), we could significantly speed up the simulation because in studies of ensemble averages of equilibrium systems, dynamics through the phase space does not need to correspond to any physical dynamics. It would be enough that the detailed balance condition between transition rates would be fulfilled and that each state can be reached. Unfortunately traditional Monte Carlo methods, like the Metropolis algorithm [54], suffer from the disadvantage that the majority of transitions are rejected in realistic systems. By using the Bortz-Kalos-Lebowitz algorithm (BKL, also called n-fold way) [8] we can avoid these rejections and perform one transition in every iteration. Since every transition is accepted, using this method the rejections have to be taken into account when we calculate the waiting time required for a certain transition. This waiting time should correspond to the time wasted by the rejections. The waiting time distribution for the configuration \( c \) is described as

\[
P(c,t) = \Gamma_c e^{-\Gamma_c t},
\]

where \( \Gamma_c \) is the total transition rate. From the previous equation we can derive the length of the time step using the inverse transform method [8]. It follows from this that the time step for a certain transition can be calculated using the following equation:

\[
t = -ln(\xi)/\Gamma_c,
\]

where \( \xi \) is a random number between 0 and 1. The total transition rate is described by
\[ \Gamma_c = \sum_{c' \neq c} \nu_{c' \rightarrow c}. \]  

(4)

Here \( \nu_{c' \rightarrow c} \) is the rate of the transition from a state \( c' \) to a state \( c \). This transition rate depends on the energetics used in the system. The BKL method uses results derived with the semi-empirical effective-medium-theory (EMT) potential to describe the energetics of particles on the surface. EMT has been found to agree reasonably well with experiments for copper (100) surfaces [55, 56].

For in-plane hopping processes on copper, the activation barriers have been found to be accurately described by the following (bond counting) approximation [56]

\[ E(A,B) \approx E_{TH} + A \times (E_{S2H} - E_{TH}) + B \times (E_{K2H} - E_{S2H}), \]

(5)

where \( E_{TH} = 0.399 \) eV is the activation barrier for terrace hopping, \( E_{S2H} = 0.258 \) eV is the activation barrier for diffusion along a step edge and \( E_{K2H} = 0.518 \) eV is the activation barrier for a jump of a kink atom to a step edge. The free parameter \( A \) has a value of one for processes where at least one of the neighbouring atoms is next to the saddle point and zero otherwise. The parameter \( B \) gives the number of nearest neighbour bonds lost in the process, \( B = \max(0, NN_i - NN_f) \) where the index \( i \) refers to the initial configuration and the index \( f \) to the final configuration. Hence the energy \( (E_{K2H} - E_{S2H}) \) can be described as the bond energy, \( E_B \), which has a value of \( 0.260 \) eV. In an earlier work [56] it has been found that the state transition theory estimates the prefactor for such processes to be in the range \( \nu_0 = (1 - 5) \times 10^{12} \) s\(^{-1} \). Since the variation of this prefactor only leads to a small modification of the strongly temperature dependent jump rates, a value of \( \nu_0 = 3.06 \times 10^{12} \) s\(^{-1} \) has been chosen for in-plane terrace jump processes. Hence, atoms of the adatoms islands have the jump rates

\[ \nu_{i \rightarrow f} = \begin{cases} \nu_0 \gamma_s e^{-\beta(NN_i - NN_f)} E_B, & NN_i > NN_f \\ \nu_0 \gamma_s, & NN_i \leq NN_f. \end{cases} \]

(6)

Here the saddle point characteristics are given by \( \gamma_s = e^{-\beta E_{S2H}} \), assuming that \( A \) has a value of 1.

Out of plane hopping can not be approximated in a similar fashion. The activation barriers for such processes have been calculated individually using EMT simulations [56].
Using these energetics we then run a global heat bath simulation of the system. After each transition the transition rates for the atoms have to be updated. This makes the BKL algorithm more complicated to implement than the Metropolis Monte Carlo method. However, examining these calculations it can be concluded that only the transition rates of the atoms within the interaction range of the initial and final positions of the occurred transition have to be updated.

![Figure 1: Overhang relaxation mechanisms at the transition from molecular dynamics to KMC. The figures are projections in the $\langle 110 \rangle$ direction. The circles in the figures represent atoms, filled circles represent overhang atoms. The numbers in the filled circles indicate in what order the overhang atom will be relaxed. In a) we have a (110) facet of the cluster; the atoms higher than 1 layer over the surface do not see the surface and have nowhere to move, thus creating an overhang. In b) we have a (111) facet of the cluster; relaxing the lowest overhang atom (labeled 1) will result in a new overhang for the next atom (labeled 2) and so on. This procedure will ultimately move the whole row of atoms to the bottom of the facet.](image)

The BKL simulation method utilises a lattice gas system, which means that the locations of atoms will be discrete in space. This is of no concern to the reliability of the MC simulation method since the atoms in and at the surface of FCC metals are spatially localised. A problem arises when we wish to combine MD methods with MC methods, e.g. how to reliably translate the positions of atoms in the continuous space of the MD to the discrete space of the MC. For this to be possible at all, we need to make sure that a translatable system does not contain amorphous zones or other non-epitaxial regions.
The work presented in paper I established a regime of cluster size versus system temperature for epitaxial growth of copper on a copper (100) surface by depositing copper nanoclusters. As long as we are within this regime we can be certain that we have a suitable system. In the MD simulations we have a free surface where the nanoclusters will be deposited and the bottom layer of the system will be fixed. Thus the bottom atoms will correspond to perfect lattice sites, i.e. directly to positions in the discrete space. Tracing the atom rows upwards from these fixed atoms allowing a deviation (15° was found to be suitable) for every atom layer we can find the height of a particular column of atoms. Doing this procedure for all the bottom layer atoms we find the height of all columns of atoms in the system.

Due to the implementation of the lattice gas system the BKL algorithm does not keep track of individual atoms below the surface. The data structures of the implementation only include the height of every column of atoms, as indicated in the previous paragraph. This significantly simplifies enumeration of configurations of the considered system, but it does also constitute a problem. The problem arises when we transfer systems from the MD simulation output, because the MD simulations allow any possible topology of the surface, whereas the used implementation of the BKL algorithm only allows height differences of one in neighbouring atom columns. We call larger height differences overhangs. To overcome this problem, the overhangs must be excluded in some physically well motivated way. It is evident that systems with overhangs will have higher energies as compared to flat surfaces since the total surface area will be larger. This indicates that it should be possible to relax the system so that the overhangs would be eliminated. We investigated this possibility by simulating systems with overhangs at elevated temperatures to accelerate the relaxation process. The result of these simulations are shown in section 5. From these simulation results we could then derive a relaxation algorithm for the systems. The algorithm procedure is illustrated in figure 1.

4.3 Particle coalescence method

The particle coalescence method (PCM) is used to simulate a system described by the island size and density distribution rate equation. Using PCM we consider a lattice, which does not correspond to any physical object, onto which we have placed islands of certain sizes. The islands are considered to be point-like, thus the geometry of the islands does not have to be considered further. The pairs of islands to aggregate or which have fragmented are chosen randomly from the lattice. This is done to satisfy the mean-field (MF) approximations of the rate equation [57].
The PCM simulation is described by the rate equation

$$\frac{dn_s}{dt} = \frac{1}{2} \sum_{i+j=s} [K(i,j)n_in_j - F(i,j)n_{i+j}] - \sum_{i=1}^{\infty} [K(i,s)n_in_s - F(i,s)n_{i+s}],$$

(7)

In this equation $n_s$ is the areal island density for islands of size $s$, the aggregation kernel $K(i,j)$ gives the probability that an island (of size $i$) will be aggregated with another island (of size $j$) and the fragmentation kernel $F(i,j)$ gives the probability that an island will be fragmented into two separate islands of sizes $i$ and $j$.

In the PCM simulation the islands undergo processes with a site on the lattice, which is randomly chosen with uniform probability. If this site is already occupied by another island, the islands will aggregate with the probability given by the aggregation kernel. If the aggregation event is accepted, a new island with the size $s = i + j$ will be formed, otherwise the islands will be left at their original sites. Fragmentation events are treated in the same way as aggregation events, except that fragmentation events are accepted with the probability described by the fragmentation kernel. The aggregation kernel $K(i,j)$ can be described as

$$K(i,j) = K_0(i^{-\mu} + j^{-\mu}),$$

(8)

where $i^{-\mu}$ and $j^{-\mu}$ are the island diffusivities for islands of sizes $i$ and $j$. $\mu$ is in the range of 1-3 [58], but in the models used we restrict the value of $\mu$ to 1 or 2. The fragmentation kernel $F(i,j)$ can be described as

$$F(i,j) = F_0'(i + j)^\alpha(\delta_{i1} + \delta_{j1}),$$

(9)

where the $\delta_{ij}$ components restrict the breakup to adatom detachment only. Due to this restriction the detachment constant on the lattice is defined as $F_0' = L^2F_0$, where $L^2$ is the size of the system (i.e. number of lattice sites) and $F_0$ is the detachment rate in number of detachments per second. The $\alpha$ parameter is assumed to have a value of 0.5, which is obtained from the simple geometrical argument that the detachment probability scales as the side length of the island. This and the functional form of the fragmentation kernel, $s^\alpha$, was confirmed by our MD simulation results presented in paper III.

If the number of lattice sites, $L^2$, is large compared to the number of islands, $N_{isl}$, the probability of moving an island to a site already occupied by another island will be very small, this will lead to a great deal of computational power solely spent on moving around the islands on the lattice. These events can be compared to the rejection of transitions in the Metropolis Monte Carlo method and can thus be eliminated in a similar fashion as in the BKL Monte Carlo method [59]. MF assumptions require that the lattice is mixed. This can be circumvented by discarding the lattice and only maintaining
a list of all islands. The simulation is then conducted by choosing an island randomly and letting it either aggregate with another randomly chosen island, fragment or undergo growth by deposition. The physical time in this case will be calculated as described in equation (3) where the rate $\Gamma$ is replaced, depending on the event, by:

$$
\begin{align*}
\Gamma_{agg} &= 2K_0N_{isl}(N_{isl} - 1) \\
\Gamma_{frag} &= \nu_{frag}^\text{max}N_{isl}(L^2 - N_{isl}) \\
\Gamma_{dep} &= L^2K_0R(L^2 - N_{isl})
\end{align*}
$$

Here $L^2K_0/R = \Phi$ is the deposition rate, $R = K_0/\Phi$ and $\nu_{frag}^\text{max}$ depends on the specific form of the fragmentation kernel. If the fragmentation kernel has the form $F(s = i + j) \propto s^\alpha(s - 1)$ and $\alpha > -1$, then $\nu_{frag}^\text{max} = F(s_{\text{max}})$, where $s_{\text{max}}$ is the size of the largest island in the system. The procedure described above increases the complexity of the implementation but has been found to speed up the simulations by a factor of up to 2000.

In order to monitor growth one must scale the island size distributions properly. The probability density that a randomly selected atom is contained in an island of size $s$ is given by $p(s; \theta) = sn_s(\theta)/\sum_{i=1}^{\infty} sn_s(\theta) = sn_s(\theta)/\theta$, where $\theta$ is the coverage. Using this probability density we can define the average size of an island as $\bar{s}(\theta) = \sum_s sp(s; \theta)$. Choosing these definitions is convenient for resolving the interesting scaling properties in this work [59–61]. In the scaling region the island size distribution scales as $g(s/\bar{s}) = \bar{s}p(s; \theta)$, which completely determines the island size distribution provided that the average size $\bar{s}$ is defined.

### 4.4 Analysis methods

It is evident that simulation results are worthless if you do not have the proper tools to extract the essential information from the vast amount of information produced by the simulation programs. The molecular dynamics program used in this thesis outputs three-dimensional components of coordinate, velocity, force, and many other parameters for every atom in the system. Without analysis tools the user has to rely on his/her skills of interpreting projections of this three-dimensional data, which certainly is not trivial. To make this task easier I have developed a number of algorithms to analyse this outputted data.

In paper I we needed an accurate method of determining which atoms were in the epitaxial phase and which were not. The simplest way of doing this would be to analyse the local neighbourhood of each atom and find the vectors to the nearest neighbours which mostly resemble the vectors to the nearest
neighbours of the substrate. A reference value for one atom can be calculated using the following formula:

\[ F_{\text{epi}} = \sum_i \min_j (\arccos | \mathbf{r}_{\text{Ideal}}^i \cdot \mathbf{r}_{\text{nn}}^j |). \]  

(11)

In this formula the ideal neighbour vectors (i.e. the nearest neighbour vectors of the substrate) are unit vectors marked as \( \mathbf{r}_{\text{Ideal}} \) and the unit vectors for each atom to its nearest neighbours are marked as \( \mathbf{r}_{\text{nn}} \). The sum is calculated over all the nearest neighbours. Since \( \arccos(x) = 0 \) when \( x = 1 \), this method of calculating epitaxiality will be non-sensitive to surfaces (where some neighbours might be missing). However, using this method for classifying atoms as epitaxial or non-epitaxial is difficult since we need to establish a critical value for \( F_{\text{epi}} \) above which the atom should be classified as non-epitaxial.

This lead me to develop a more accurate method of determining the lattice that an atom is a part of. The problem of deciding when an atom is a part of the epitaxial phase is identical to the problem of deciding whether the atom belongs to the same lattice as the substrate. We first calculate the vectors to the atoms at the approximate distance of one lattice constant in the case of a perfect lattice, for every atom. From these vectors we then find three vectors which form the most optimal orthogonal set. When this orthogonal set of vectors has been defined for all atoms in the system we group the atoms depending on these vectors. Within every group we only allow a certain deviation of the vectors from the mean values of the vectors for the group. If the deviation is higher than a critical value we form a new group. This gives us a method to accurately define the lattice to which a certain atom belongs, assuming that we can choose the critical values correctly. This method also proved to be valuable when determining the movement of the nanocluster studied in paper IV. The nanocluster was found to be rotating slightly, due to the fact that it was single crystalline all the atoms in the nanocluster were defined by the same set of orthogonal vectors and the rotational angle of the cluster could easily be calculated.

In the work described in paper IV we also needed a method of detecting mobile dislocations in the system. A method for this has already been developed in an earlier work [62]. The general idea of this method is that you determine the nearest neighbours for each atom in the initial system. The method then analyses the neighbourhood of each atom and tries to identify six pairs of opposite neighbours relative to the analysed atom. The centrosymmetry parameter is described with the following formula:

\[ P = \sum_{i=1,6} \left| \mathbf{R}_i + \mathbf{R}_{i+6} \right|^2. \]  

(12)
Here the vectors to the opposite pair of atoms are noted as $\mathbf{R}_i$ and $\mathbf{R}_{i+6}$. You then follow the change of $P$ using the same set of neighbouring atoms. Unfortunately this method has the disadvantage that it is not possible to determine the type of the dislocation solely on the value of $P$. This is why I introduced the use of the centrosymmetry vector, which is defined as

$$ P = \left( \sum_{i=1,6} \mathbf{R}_i + \mathbf{R}_{i+6} \right) / 8. $$

The change of this vector will show the direction of the dislocation movement and the relative movement of the local neighbourhood. The vector is scaled by a factor of 8 to approximatively compensate for the number of atoms and the relative distance of these atoms, hence the length of the vector will describe the distance the atoms have moved in order to form the dislocation. By visualising the vectors at the original position of the atom, edge and screw dislocations could easily be recognised as forming rows or planes depending on the type of dislocation.

## 5 NANOCLUSTERS ON SURFACES

Using nanoclusters in any real application will at some point include interaction of a nanocluster with a surface. The nature of the interaction will depend on several factors; interaction on the atomistic level, kinetic energy of the nanocluster, structural integrity of the nanocluster, substrate and nanocluster temperature.

The interaction between the surface and a deposited nanocluster manifests itself in several ways. If the structural integrity of the nanocluster cannot withstand the forces between the nanocluster and the surface, as is the case of a copper nanocluster on a copper surface, these forces will modify the structure of the nanocluster. The main driving force for this modification is the minimisation of the total surface energy for the whole system. Figure 2 shows the potential energy evolution of copper nanoclusters during deposition on copper (100). It is evident that the shape of the nanocluster undergoes change even up to 5 ps after the deposition event.

Once the nanocluster has been deposited onto the surface the surface energy of the nanocluster is large. In order to minimise the total energy of the system, it strives towards optimising the surfaces. The surface energy released due to the lowering of the surface of the nanocluster will lead to heating of the local area around the nanocluster which potentially leads to even further modification of the
Figure 2: Average potential energy for the atoms of Cu clusters and the Cu substrate as a function of time for deposition at 0 K. The 6, 13 and 19 atom clusters were within the size limit for epitaxiality, whereas the 38, 55, and 79 atom clusters were not. $E_0$ is the average potential energy of an epitaxial system.

Figure 3: Snapshots of a cubic nanocluster on the a copper surface. The snapshots are viewed in the $\langle 110 \rangle$ direction of the system. Snapshot (a) shows the initial configuration of the system, (b) and (c) show the configuration of the system after simulating the thermal movement of the atoms for 2 ns at 800 K with molecular dynamics, starting with different configurations for the initial velocities of the atoms.

Figure 4: Snapshots of a pyramidal nanocluster on the a copper surface. The snapshots are viewed in the $\langle 110 \rangle$ direction of the system. Snapshot (a) shows the initial configuration of the system, (b) and (c) show the configuration of the system after simulating the thermal movement of the atoms for 2 ns at 800 K with molecular dynamics, starting with different configurations for the initial velocities of the atoms.
structure. Figures 3 and 4 show how this minimisation will modify the structure of a cubic and a pyramidal copper nanocluster on a copper (100) surface.

In this section I discuss the results obtained for nanoclusters at surfaces that were reported in papers I, II and III.

5.1 Thin film growth by nanoclusters

From experiments on nanocluster deposition on surfaces it is known that upon impact nanoclusters may become completely epitaxial with the substrate [63, 64]. This phenomenon is called contact epitaxy. Whether we have full contact epitaxy or not, will directly reflect on the quality and type of the grown film. The quality and type of the film can easily be controlled by choosing the temperature of the substrate, the size distribution of the deposited clusters, and the flux during deposition.

![Figure 5: Snapshots of the annealing of a 711 Cu atom cluster at a) 40 ps b) 900 ps after the landing. The substrate temperature is 600 K. In a) the cluster has a grain boundary in the upper right corner, which has been annealed in b).](image)

The mechanism behind contact epitaxy can be easily understood. Low substrate temperatures will cause the nanoclusters to have less tendency of annealing defects and grain boundaries after deposition (shown in figure 5) and thus creating nanocrystalline films. However, the smaller the deposited clusters are, the lower the activation energy is for this annealing process. This implies that there is a regime of substrate temperature versus size of the deposited nanoclusters where full contact epitaxy is always achieved. Figure 6 shows the regime established with our MD simulations of the deposition of a single nanocluster of different sizes onto substrates at different temperatures.

If the flux during deposition is increased, the deposited nanoclusters will start to interact with nanoclusters already deposited. This affects the contact epitaxy by lowering the size of nanoclusters that
undergo full contact epitaxy at a certain temperature [65]. Allowing the clusters to relax at the surface will reduce the clusters into monolayers as will be shown in section 5.3. This procedure creates an environment for the next deposited nanocluster which is essentially identical to a flat surface, thus increasing the probability of full contact epitaxy. Using cluster sources of today [66] this becomes important at temperatures of 400-500 K where the relaxation time is of the same order as the interval between deposition events in the same local area.

5.2 Nanocluster deposition process

When a nanocluster enters the vicinity of a surface the atoms of the nanocluster start to interact with the atoms of the surface. Due to this interaction the nanocluster will accelerate toward the surface and impact on the surface with a large kinetic energy as compared to thermal energies (~ 20 meV/atom). This acceleration is caused by the release of energy, due to the lowering of the surface energy of the system [63]. This release of energy will lead to a temperature raise of the order of one thousand Kelvins in the local area around the cluster. This will increase the probability of full contact epitaxy as can be seen in the low temperature end of figure 6, as the fitted line does not intersect the origin. The amount of the released energy during the landing can be estimated from figure 2, considering that the substrate contained 1134 atoms.

If the deposited nanocluster has a kinetic energy which is considerably higher than thermal energies, the deposition of the nanocluster will cause large scale damage in the substrate and the atoms of the
nanocluster will enter deep into the substrate. This is a completely different field of research and is outside the scope of this thesis.

### 5.3 Transformation of deposited nanoclusters to monolayer nanoclusters

Relaxing a copper nanocluster on a copper (100) substrate on a long enough time scale shows that the nanocluster will be reduced to a monolayer on the surface. This configuration has the lowest possible surface energy for (100) surfaces, unfortunately this reduction process is very slow due to a high activation barrier. This makes MD a very inconvenient method for studying this process. However, it is possible to study it partially by supplying enough activation for the process, for instance by heating the substrate. The partial study of this process using MD can be seen in figures 3 and 4.

Using the BKL KMC method described in section 4.2 we could simulate these systems on time scales up to thousands of seconds. We observed that a nanocluster will be reduced by breaking up the top layer by atom detachment from the step edge which then moves down to lower terraces. Once the whole top layer has been transferred downwards, the following top layer will start to undergo the same process, and this goes on until the whole nanocluster has been reduced to a monolayer.

![](image)

**Figure 7:** Time required for the initial relaxation as well as the reduction to one monolayer of clusters of sizes 413, 851 and 2045 atoms at a certain temperature. The data for the clusters has been calculated as an average over 10 simulations and the lines have been fitted to the data assuming an Arrhenius behaviour. Also shown is the MD simulated relaxation result calculated for a cube on the surface consisting of 726 atoms, which can be seen in figure 3.

The most interesting fact about this process is how long it takes for a nanocluster to be reduced to a monolayer, i.e. how large the interval between cluster deposition events in the same local area must
be to have maximum probability of full contact epitaxy. Figure 7 shows the times required for clusters of different sizes at different temperatures to undergo this process, based on the data it is clear that it has an Arrhenius behaviour. The figure also shows the time required for the relaxation algorithm described in section 4.2. This was estimated by observing the behaviour of the relaxation process in the MD simulations at different temperatures and was found to have an activation energy of $0.18 \pm 0.05$ eV. From this estimated data it is evident that the relaxation process will not interfere with the determination of the reduction time.

![Graph showing activation energy vs. cluster size](image)

**Figure 8**: a) shows the effective activation energy as a function of the nanocluster size. The grey line shows the activation energy for the detachment of one atom from a straight step edge, called K1H [56]. The K1H process is shown schematically in b).

From the time data we can easily calculate the activation energy data of the whole reduction process. Figure 8 shows the activation energy as a function of the nanocluster size. Although the activation energy only varies over an interval of about 0.15 eV, a systematic size dependence is observed. Examining the occurrence of different atomistic processes for different sizes of clusters showed that dimer formation and dissociation is more common for clusters containing 22 and 46 atoms as compared to larger clusters. We believe that this is the reason for the higher stability of the small clusters. In the same examination it was concluded that clusters consisting of 22-107 atoms have a higher occurrence of downward atom movements over several layers at corners of the nanocluster, with a maximum for clusters of 107 atoms. This downward movement has an activation energy of 0.66 eV which explains the dip for the activation energy with a minimum for clusters consisting of 107 atoms.
Comparing the activation energy of the reduction process to the activation energy of the K1H process, i.e. the detachment of an atom from a straight step edge (0.87 eV), we can see that for clusters larger than 50 atoms the largest deviation is about 0.07 eV. Since K1H is the only process with an activation energy within this interval, we can conclude that this process has a significant role in the reduction process. This is quite evident if we consider the observed behaviour of the reduction process since the local neighbourhood seen by one atom will often resemble a straight step edge.

The findings of paper I and II can be used for determining parameters such as the size of the deposited clusters, substrate temperature, and the deposition flux to be used in cluster deposition experiments depending on the desired properties of the grown film.

### 5.4 Breakup of monolayer nanoclusters

Bombardment of cobalt monolayer nanoclusters on a silver (100) surface with cobalt atoms with kinetic energy in the range of 5-30 eV will damage the nanocluster. The kinetic energy of the incoming ion is low enough to limit the damage to the surface layer. However, it is high enough to induce breaking up of the cobalt nanocluster. By analysing these breakup events it is possible to calculate the $\alpha$ parameter (equation 9) of the fragmentation kernel used in the PCM method. Bombarding the whole surface evenly and calculating the fragmentation probability for this, proved to give very poor statistics. By limiting the bombarded surface we could obtain much better statistics. We tried two different types of limitations, we called these 20 % and 100 % relative bombardment areas. Using the 20 % relative bombardment area we allow bombardments over an area five times the size of the nanocluster, centered on the nanocluster. In this case the nanocluster will be hit by 20 % of the incoming atoms giving good statistics for processes involving both the nanocluster and the uncovered surface. In the 100 % relative bombardment area case we only bombarded the surface area covered by the nanocluster and thus maximize the statistics of processes involving the nanocluster. The detachment probability, i.e. the probability the one atoms fragments from the nanocluster, is shown in figure 9 for both cases. From this figure it can be seen that the detachment probability for the 100 % case is approximately five times the probability of the 20 % case, as should be the case if the limitations are chosen correctly.

From the detachment probabilities gained in the simulations the value of the $\alpha$ parameter could be calculated. It is known that the detachment probability should behave as $s^\alpha$ where $s$ is the size of the island. For the 20 % relative bombardment area, the value was found to be $0.38 \pm 0.16$ and for the 100 % relative bombardment area $0.52 \pm 0.03$. Previously the value of $\alpha$ has been assumed to have a value of 0.5, which our simulation results thus confirm.
Figure 9: Probability of detachment of Co atoms from the Co island for the configurations with 20 % and 100 % relative bombardment area. A curve with a function of $F(s) = F_0 s^\alpha$ has been fitted to the data, where $F_0$ is a scaling factor and $s$ the size of the island.

Based on recent experiments on growth of Co on Ag (100) using LEID [67] it was suggested that the mechanism behind the high island density would be dissociation of the monolayer nanoclusters upon bombardment. Nevertheless, in the MD simulations we did not observe a single dissociation event of a Co island. The PCM simulations gave island densities which were in very good agreement with the measured island densities. Since the PCM simulations were limited to atom detachment we can conclude that high island density is due to the enhanced detachment of adatoms, and the consecutive detachment or fragmentation events induced by the incoming ions.

6 NANOCLUSTERS BELOW SURFACES

Nanoclusters are not only found in vacuum or on surfaces, they can also be found partially or completely embedded in a substrate. Whether nanoclusters are crystalline or amorphous, consist of the same material as the substrate or not, they will interact with their surroundings. Crystalline embedded nanoclusters have been found to align with the substrate lattice if the difference of the lattice constant of the nanocluster material and the substrate material is less than $\sim 3 \%$ [31, 68]. Amorphous nanoclusters will undergo recrystallisation during thermal treatment or irradiation by ions, laser beams or electrons.
6.1 Nanocluster burrowing below the surface

Recent experiments [29, 30] have shown that Co nanoclusters thermally deposited on Cu (100) or Ag (100) will burrow into the surface when thermally activated. The experiments also showed that the clusters align with the substrate during burrowing, although the time or space resolution of these experiments was not good enough to observe the actual mechanism of the burrowing process, and how and when the alignment occurs.

In the work of paper IV we examined this process by thermally depositing Co nanoclusters in the size range of 2-5 nm in diameter onto the surface and allowed them to relax on the surface. Nanoclusters with a diameter of ~ 2 nm were found not to have enough structural integrity to withstand the forces at the surface and underwent full contact epitaxy upon deposition. This procedure seemed to prevent any burrowing as none could be observed starting from these configurations. For nanoclusters that had sizes larger than ~ 2 nm in diameter we observed that the ones landing on a facet, with the same surface configuration as the substrate, lock on to the surface and slowly start to burrow. Nanoclusters landing on other facets were observed to move around on the substrate, trying to find a minimum energy configuration with the surface. Lowering the substrate temperature lead to the locking of a \(<110>\) direction of the \(<111>\) facet to a \(<110>\) direction of the substrate surface. No burrowing could be observed for nanoclusters of this orientation.

By analysing the epitaxially landed nanoclusters on the surface we could observe burrowing. Through analysis of the movement of vacancies during this scenario we could observe an enhanced activity along the Co-Cu interface of the nanocluster and the substrate. This enhanced activity was due to the tensile stress at the interface. The vacancies were found to enter on the Cu side of the interface and exit on the Co side, thus leading to a mass transport with the net effect of burrowing of the nanocluster.

The most interesting behaviour was observed for nanoclusters that landed on a corner or an edge, an example of this type of configuration can be seen in figure 10 a). In this case the strong attractive forces lead to a very rapid pulling phase in the burrowing as can be seen in the first 5 ns of figure 11.

We simulated the burrowing process for the nanocluster shown in figure 10 up to 140 ns. The progress of the burrowing is shown in figure 11. As can be seen from this figure the burrowing stops after about 70 ns. At this point the surface of the nanocluster had formed a stable interface with the substrate, the \(<221>\) plane of the nanocluster matched up with the \(<100>\) plane of the substrate. Earlier we had observed that during burrowing the nanocluster slightly moves around and this was apparently coupled to the burrowing process. After the locking we observed the same vacancy driven burrowing mechanism as for the epitaxially landed nanoclusters.
Figure 10: The series of figures show how a nanocluster landed on a corner starts to burrow into the substrate. The figures are cross sections of a chosen part of the whole lattice to clarify the burrowing process. Figure a) shows the configuration when the nanocluster has relaxed on the surface, b) how the nanocluster has burrowed after 20 ns and c) the situation after 60 ns.

![Diagram of nanocluster burrowing](image.png)

Figure 11: Degree of burrowing for a nanocluster. Three different phases of the burrowing process can be observed in the figure, the first fast pulling phase lasts about 2 ns from the beginning of the simulation, then the slower rotational phase takes over, which lasts for about 70 ns until the (221) plane of the cluster matches up with the substrates (100) plane and the very slow vacancy migration burrowing phase starts.

![Graph of time vs. number of atoms](image.png)

Through analysis of the movement of the nanocluster using the lattice analysis algorithm described in section 4.4 the rotational angle of the nanocluster could be determined. Figure 12 shows that the rotation was directed in such a way that the nanocluster would reach a more aligned (i.e. lower average $F_{\text{epi}}$ value for the atoms of the nanocluster) configuration. Using the dislocation analysis algorithm we could assure ourselves that the rotation was real and not due to dislocation propagation through
Figure 12: a) shows the epitaxfactor, $F_{epi}$, and c) the rotational angle for the cluster during the simulation. The rotational angle is calculated as the angle between the initial $\langle 001 \rangle$ direction of the cluster and current $\langle 001 \rangle$ direction at a given time. b) and d) show the movement of atoms during the intervals shown in the graphs. The bars in b) and d) represent the movement of one atom during an interval of 1 ns. To avoid cluttering of the atom movement figures, only atom movements between 1.5 Å and 5 Å are shown. Note that the atom movement in d) gets longer outwards from the center of the cluster, this is consistent with a rotation and not with a dislocation movement. Interval (A) corresponds to a time of 1 ns and interval (B) corresponds to a time of 3 ns.

The mechanism for the burrowing in this case, i.e. for nonaligned nanoclusters, was found to be disordered motion of atoms along the Co-Cu interface.

To summarize the findings on burrowing, we observed three different phases of Co nanocluster burrowing into a Cu (100) substrate. The fastest one was the rapid pulling phase which was due to the strong attractive forces between the facets of the nanocluster and the surface. This phase only occurred if the nanocluster had landed on an edge or a corner. Once the nanocluster had been pulled in as far as possible, the second phase of the burrowing was commenced by disordered movement of Cu atoms...
along the Co-Cu interface. When the nanocluster reached an aligned configuration with the surface, the third and slowest phase of burrowing was observed. In this phase the burrowing was due to vacancy movement along the Co-Cu interface with the net effect of a mass transport of Cu atom from beneath the nanocluster to the surface.

### 6.2 Amorphous nm-sized inclusions

Experiments with the aim of observing amorphous nanoclusters in semiconductors using transmission electron microscopy (TEM) have shown that subjecting the sample to the electron beams of the measurement equipment induce a recrystallisation of the nanoclusters. By implanting an As atom with a kinetic energy of 5 keV we created damage in a Si substrate similar to the one examined in the experiments. Applying the non-bonding bond-breaking, anti-bonding bond-breaking and local heating events described in section 4.1 at the amorphous-crystalline interface we observed different recrystallisation behaviour. As a reference we simulated the same scenario at an ambient temperature of 300 K to analyse the possible spontaneous recrystallisation [V].

![Graph: Number of atoms in the amorphous phase during the simulation for the different models with the Tersoff potential 300 K as well as one simulation at 0 K.](image)

The results for the recrystallisation can be seen in figures 13 and 14. The speed of the recrystallisation in the bond-breaking simulations ranged from 4.2 to 11.1 atoms per 100 bond-breaking events with the Tersoff potential depending on the used recrystallisation mechanism model and parametrisation. With the Stillinger-Weber potential non-bond model the recrystallisation speed was about 1 atom per 100 bond-breaking events. For the Tersoff model reference run, with the total simulation time of 2
ns, the recrystallisation of the amorphous nanoclusters is 2.8 %. This equals a recrystallisation speed of about 1 atom per the time corresponding to 100 bond-breaking events, i.e. much less than that in the bond-breaking simulations. However, the majority of this recrystallisation occurs during the first 0.5 ns (1.6 %). The phenomenon of slowing down of thermal recrystallisation after the lattice has relaxed has also been observed in other simulations [69]. Similar behaviour could be observed for the Stillinger-Weber potential simulation, where the recrystallisation speed was about 0.2 atoms per the time corresponding to 100 bond-breaking events, again much less than that in the bond-breaking simulations. In the Stillinger-Weber case it could be observed that all of the recrystallisation is due to the sudden recrystallisation of small amorphous nanoclusters. From an additional reference run at 1000 K we observed that approximately 4.2 atoms recrystallised in a time corresponding to 100 bond-breaking events.

An atom was determined to belong to the amorphous nanocluster if the potential energy of the atom was 0.2 eV higher than the potential energy of a Si atom in a perfect lattice. To be certain that the lowering of the potential energy analysis method actually described the recrystallisation and not some internal relaxation of the amorphous areas, one must visually examine the crystal structure. An example of the change of the amorphous nanocluster is shown in figure 15.

The models we used for this study insert a maximum energy of $3.4 \times 10^{-2}$ eV. In earlier work the threshold energy for thermal recrystallisation was suggested to be 0.8-1.0 eV [70]. It seems unlikely that heating alone could be the reason for the observed recrystallisation. To rule out any temperature dependence of the recrystallisation for the bond-breaking, we also ran the anti-bond bond-breaking
Figure 15: Initial and final (after 9000 bond-breaking events) lattice of the Stillinger-Weber non-bond simulation. Only a specific part of the whole lattice is shown in this figure.

simulations at 0 K. The results for these simulations are practically identical with the results for the simulations conducted at 300 K. The results of the hot spot simulations also confirmed this. Hence we can conclude that the recrystallisation is mainly due to geometric rearrangement of the atoms while the bond is broken.

The Spaepen-Turnbull model [38] explains recrystallisation during irradiation with migration of dangling bonds along the amorphous-crystalline interface which lead to a more energetically favorable configuration of the atoms. This model proposes that some additional thermal activation is required for the recrystallisation to occur. However, simulations using our bond-breaking model show recrystallisation at 0 K, which is in good agreement with experiments that show recrystallisation at temperatures as low as 30 K [37]. This shows that the Spaepen-Turnbull model does not describe the recrystallisation process entirely correctly.

7 CONCLUSIONS

We have studied the kinetics of nanoclusters on surfaces and in thin films using molecular dynamics, kinetic Monte Carlo and particle coalescence methods. The methods have been presented along with the extensions required for successful application to the studied systems. Analysis tools required for the extraction of the essential information were also presented.
The deposition of Cu nanoclusters onto a Cu (100) surface was studied and a cluster size versus substrate temperature regime was established for epitaxial growth of thin films. The evolution of a Cu nanocluster on a Cu surface was studied at long timescales and the activation energy for the relaxation process was found to depend on the nanocluster size. It was found that for clusters consisting of more than 300 atoms the atomistic process of atom detachment from a straight step edge plays a dominating role in the evolution. These results can be used to estimate deposited cluster size, substrate temperature and deposition flux for manufacturing epitaxial or nanocrystalline thin films.

The functional form of the fragmentation kernel and the value of the $\alpha$ parameter used in it were determined with MD simulations of Co island breakup during Co irradiation. The value of $\alpha$ was determined to be $0.52 \pm 0.03$, this is consistent with the previously assumed value of 0.5. PCM simulations of the irradiated island showed that the island size and density distribution observed in experiments can be successfully explained based on the consecutive detachment of Co atoms from the islands.

The behaviour of Co nanoclusters during deposition and the relaxation of them on a Cu surface was presented. We found two different main mechanisms depending on the orientation of the nanoclusters after landing. Epitaxially landed clusters were found to burrow by vacancy migration along the Co-Cu interface while non-aligned clusters burrowed by disordered motion of atoms along the Co-Cu interface.

Recrystallisation of amorphous nanocluster in Si thin films was studied using a bond-breaking model we developed. The simulations using the bond-breaking model reproduced the recrystallisation behaviour seen in experiments at different temperatures, and showed that no thermal activation is necessary for recrystallisation.

Taken together, this thesis presents the use of computational methods for studying nanocluster evolution during deposition, thermal activation, and irradiation with ions or electrons. The obtained results can be used in the development of novel manufacturing or modification processes for epitaxial and nanocrystalline materials.
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Jonas Frantz
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