Evolution of Cu nanoclusters on Cu(100)

J Frantz, M Rusanen, K Nordlund and I T Koponen

Accelerator Laboratory, PO Box 43, FIN-00014 University of Helsinki, Finland

E-mail: frantz@acclab.helsinki.fi

Abstract
Using molecular dynamics simulations combined with kinetic Monte Carlo
methods we have studied the evolution of copper nanoclusters on a copper (100)
surface. We have developed a method for relaxing the clusters into a suitable
configuration for input into the kinetic Monte Carlo method using molecular
dynamics. Using kinetic Monte Carlo methods we have simulated the evolution
of clusters with sizes of 22–2045 atoms at temperatures of 220–1020 K. We
found that the Cu clusters on the surface will be reduced to one monolayer if
given enough time to relax, and that this process shows an Arrhenius behaviour.
In this paper we present the relaxation method that we developed and our
observations for the evolution of the clusters.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Interest in completely epitaxial growth of materials has risen due to the growth of the
microelectronics field. Fast, reliable methods of growing epitaxial as well as nanocrystalline
thin films are required to satisfy the needs of the rapid production process for microelectronic
components (Müller *et al* 1997, Blackburn *et al* 2001). Using nanocluster deposition for thin
film growth could potentially provide a method with a wider set of adjustable experimental
parameters than with thermal deposition of single atoms.

Experiments have established that when a small enough cluster lands on a single-crystalline
substrate, the lattice of the cluster will align completely epitaxially with the substrate upon
impact (Ghaly and Averback 1993, Yeadon *et al* 1999). This process can be called e.g. contact
epitaxy (Yeadon *et al* 1999). When using this technique to grow thin films, a problem arises
when one wants to optimize the growth speed by enlarging the deposited clusters. Earlier
work has shown that (Meinander *et al* 2003) as nanoclusters grow in size they react more
slowly, due to the lowering of the surface area to volume ratio. This can be compensated for
by adding some activation to the system by heating it. A cluster size–temperature regime for

full contact epitaxy of Cu clusters upon deposition on a Cu surface was established in this work (Meinander *et al* 2003). As long as we are within this regime, the system can, without complications, be simulated in a discrete space. It is important to realize that the evolution of the cluster on the surface plays an important role for the growth of the surface as more clusters are deposited on top of it. Other work on this area (n.d.a.—Meinander *et al* 2004) shows that secondary clusters deposited on top of existing clusters at the surface have smaller probability of obtaining a epitaxial structure than the primary clusters deposited on a flat surface. Allowing the primary clusters to smooth out before depositing a new cluster in its vicinity could result in high quality epitaxial thin films. Optimizing the speed of the growth requires that we know how long it takes for a cluster of a given size to be smoothed out at the surface at a certain temperature.

To analyse the smoothing out of the cluster at the surface, one must analyse the evolution of the system on a timescale of the magnitude of seconds. Due to this fact a pure molecular dynamics method is not suitable. This leads to us utilizing a faster type of simulation scheme, the optimal choice being a lattice Monte Carlo method. The method of choice in this work is the Bortz–Kalos–Lebowitz (BKL) (n.d.b.—Bortz *et al* 1975, Kotrla 1995, Blue *et al* 1995) method, due to its high efficiency and versatility.

Our implementation of the BKL Monte Carlo method is surface oriented, so there is no way of defining the configuration of the bulk. As we try to merge molecular dynamics with this scheme, we face the problem of overhangs at the surface. This problem arises from the fact that when a cluster is deposited on the surface with molecular dynamics, pockets may be formed between the cluster and the surface. The atoms above these pockets will form overhangs and overhangs cannot be treated in a reasonable physical way by our implementation of the BKL Monte Carlo scheme. This calls for a relaxation algorithm for the cluster so that any arbitrary configuration of a cluster on the surface can be transformed to one without overhangs.

In this paper we describe the overhang relaxation and cluster reduction to a single-monolayer mechanism and predict the timescale for both processes. The result can be directly used to determine suitable nanocluster deposition fluxes in experiments and also provide a basis for further simulation work.

2. Computational details

For this work both molecular dynamics and Monte Carlo methods were used. The molecular dynamics methods were primarily used to confirm the method of relaxation for clusters with overhangs on the surface, which then could be used to develop a relaxation algorithm for arbitrary clusters on the surface. The Monte Carlo method is used for simulating the evolution of the cluster on a long timescale. The Monte Carlo simulations are also used to calculate the effective activation energy for the evolution. This is done by simulating the time that is required for a cluster to be reduced to a single monolayer.

2.1. Molecular dynamics method

Identification of the mechanisms responsible for the relaxation processes of a cluster on the surface was done by placing a cluster with the shape of a cube (with only $\langle 100 \rangle$ plane sides) or a four-sided pyramid (with only $\langle 111 \rangle$ plane sides) on a (100) surface. The evolution of the system was then simulated for up to 4 ns at 800, 900 and 1000 K to accelerate the relaxation. 800 K was shown to be a high enough temperature to allow the mechanisms responsible for the relaxation to be observed.

The size of the used simulation cell was three times the size of the clusters and periodic boundaries were used in the directions of the surface plane, while the bottom three layers

in the direction of the surface normal were fixed. The Berendsen temperature control algorithm (Berendsen *et al* 1984) with a time constant of 300 fs was used to stabilize the temperature. To describe the Cu atom interaction we used the embedded-atom-method (EAM) potential given by Foiles (1985).

The resulting atom configurations and the process statistics were analysed visually.

2.2. Kinetic Monte Carlo method

For the MC algorithm we have employed the Bortz–Kalos–Lebowitz updating scheme (n.d.b.— Bortz *et al* 1975, Kotrla 1995, Blue *et al* 1995) which allows one to reach fully macroscopic timescales around room temperature and which has also been used in previous works (Heinonen *et al* 1999, n.d.c.—Rusanen *et al* 2001). For the relevant hopping energies we use a parametrization based on the effective medium theory (EMT) (Merikoski *et al* 1997) for Cu(001). The barriers for processes on a stepped surface and their relative ordering are determined from the EMT model. They have been found to be in good agreement with the available experimental data for copper (Merikoski *et al* 1997, n.d.d.—Giesen 2001). For instance, the barrier for atom detachment from a straight step edge is 0.87 eV (process K1H if Merikoski *et al* (1997)). The barriers used in the simulations for processes on a flat surface follow a simple bond-counting rule where the rate of hopping of an atom to a vacant NN site can be approximated by (Merikoski *et al* 1997) $\nu = \nu_0 \exp\{-\beta[E_s - \min(0, \Delta_{NN})E_B]\}$, where the attempt frequency $\nu_0 = 3.06 \times 10^{12}$ s^{-1} and the barrier for the jump of a single adatom on a flat surface is $E_s = 0.399$ eV. When there is at least one atom diagonally next to the saddle point the barrier is reduced to the value $E_s = 0.258$ eV. This leads to fast diffusion along the close-packed step edges in the present case. The change in the bond number $-3 < \Delta_{NN} < 3$ is the number of nearest neighbour (NN) bonds in the final site less the number of NN bonds in the initial site. Finally, the bond energy is given by $E_B = 0.260$ eV. We note that this parametrization has been previously used to study adatom island diffusion on Cu(001) (Heinonen *et al* 1999) and molecular beam epitaxy (MBE) growth on stepped Cu(1, 1, *m*) surfaces (n.d.c.—Rusanen *et al* 2001, n.d.e.—Rusanen *et al* 2002).

Some modifications of the kinetic Monte Carlo program were necessary before we could utilize it in the current problem. An initial configuration conversion layer had to be added to enable us to import the output from the MD program, which consists of continuous coordinates, into the MC program as the initial configuration, which must consist of discrete coordinates. A relaxation algorithm was added to solve the problem of overhangs in the system. Two different types of overhang and their relaxation are illustrated in figure 1.

The initial configuration conversion layer is necessary because the MC program can only handle discrete coordinates and because it is only 'aware' of the surface of the system. The method used for the conversion identifies the bottom atoms of the system since these are usually fixed in the MD simulations and thus not subject to translation due to thermal movement. After identifying the bottom atoms the program traces each of the atom rows upwards, allowing for a 15° deviation from the surface normal at each atom step. When no more atoms can be found above the last traced atom, it is designated the surface atom for the coordinate decided by the position of the bottom layer atom. When all the bottom atoms have been traced, a final check is commenced to make sure that no atoms have been left out. If atoms are found to be left out it is usually a sign of some non-epitaxiality in the system. This is not a problem if it is a case of a few atoms at the surface, but if large numbers of atoms are left out, it is usually a sign of dislocations beneath the surface or large non-epitaxial areas at the surface. If large numbers of atoms are discarded, the system imported into the MC program might not correspond to the output of the MD program. Such configurations were not present in the clusters studied
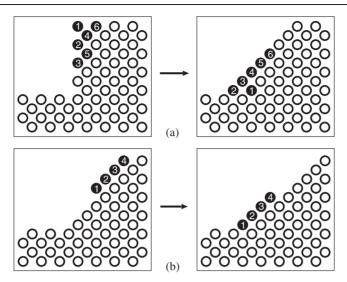
Figure 1. Overhang relaxation mechanisms at the transition from molecular dynamics to the KMC case. The figures are projections in the ⟨110⟩ direction. The circles in the figures represent atoms; filled atoms represent overhang atoms. The numbers in the filled atoms indicate in what order the overhang atoms will be relaxed. In (a) we have a 110 facet of the cluster; the atoms more than one layer above 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 (labelled 1) will result in a new overhang for the next atom (labelled 2) and so on. This procedure will ultimately move the whole row of atoms to the bottom of the facet.

in this work. However, a relaxation algorithm is necessary since the cluster imported into the MC program might contain overhangs which the MC program is not capable of handling. The mechanisms responsible for the relaxation are presented in section 3.1. The algorithm identifies the overhangs and moves the atom at the top of the overhang to the bottom. Going through this until no more overhangs are present in the system will artificially accomplish the same thing as the relaxation in the MD method.

Once the problem with the overhangs was solved we started simulating clusters of different sizes on the surface at different temperatures. The clusters had the shape of a pyramid with ⟨111⟩ plane sides and the size of the clusters ranged from 22 to 2045 atoms. As described above, the molecular dynamics simulations showed that a cluster of any shape would transform into an approximate pyramidic structure. The temperatures ranged from 220 to 1020 K with steps of 80 K or less. The program was set to stop running after the cluster had been reduced to one monolayer and the time required for this process was noted. This procedure was then repeated ten times for each cluster size and temperature; an average time and its standard deviation from this time was calculated.

3. Results

3.1. Relaxation of the cluster

Molecular dynamics simulation results of the evolution of a cube on the surface with five different initial inertia configurations are shown in figure 2. In this case the atoms located at the top corners and edges are the atoms which first move to the cluster–surface edge. This process continues until the cluster reaches a stable shape, consisting of a top ⟨100⟩ and side ⟨111⟩ planes. Excess atoms will move down the ⟨111⟩ sides until they reach the surface.

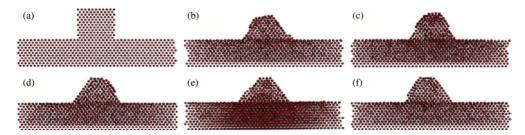**Figure 2.** Snapshots of a cubic nanocluster on the a copper surface. The snapshots are viewed in the ⟨110⟩ direction of the system. The top left snapshot (a) shows the initial configuration of the system. The other pictures show the configuration of the system after simulating the thermal movement of the atoms for 2 ns at 800 K with molecular dynamics, starting with different configurations for the atoms' initial velocity.
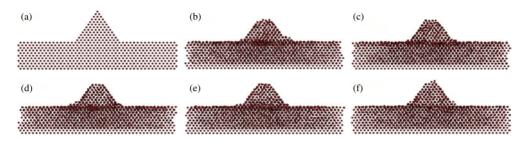

Figure 3. Snapshots of a pyramidic nanocluster on the a copper surface. The snapshots are viewed in the ⟨110⟩ direction of the system. The top left snapshot (a) shows the initial configuration of the system. The other pictures show the configuration of the system after simulating the thermal movement of the atoms for 2 ns at 800 K with molecular dynamics, starting with different configurations for the atoms' initial velocity.

After the stable shape was reached, only a few additional transitions could be observed. At this stage the relaxation was considered to have ended and the time was noted.
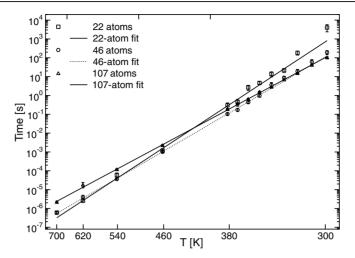
The simulation results of the evolution of a pyramid on the surface with five different initial configurations are shown in figure 3. Since the pyramid already consists of ⟨111⟩ sides, the only thing that happens is that the top atoms of the cluster relax down to the base of the cluster. Thus the pyramid reaches the same kind of stable configuration as in the case of the cube on the surface.

Examining the time required for the relaxation process for a cube consisting of 726 atoms at 800, 900 and 1000 K and fitting these data to an Arrhenius curve, the activation energy of the process was determined to be 0.18 ± 0.05 eV and the prefactor to be 0.125 ± 0.090 ns.
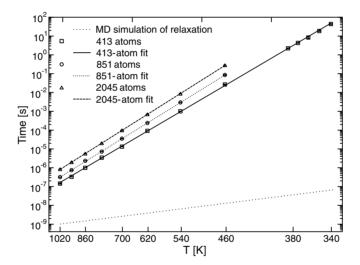
3.2. Evolution of the cluster

Some initial observations could be made from the BKL simulation of clusters at the surface at different temperatures. At 220 K the clusters did not undergo any substantial transformation at timescales up to 600 s. Therefore simulation at 220 K was abandoned and 300 K was chosen to be the low temperature limit.

Figures 4 and 5 show the time that is required for a cluster of a certain temperature to be reduced to one monolayer at the surface. From these figures it is clear that the process has an Arrhenius behaviour. From the fit of a line to the data, the activation energy and prefactor can be calculated. These are shown as a function of the cluster size in figures 6 and 7.
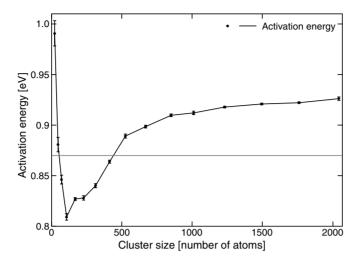
Figure 4. The time that is required for the initial relaxation as well as the reduction to one monolayer for clusters of sizes 22, 46 and 107 atoms at a certain temperature. The data for the clusters have been calculated as averages over ten simulations and the lines have been fitted to the data assuming an Arrhenius behaviour.

Figure 5. The time that is required for the initial relaxation as well as the reduction to one monolayer for clusters of sizes 413, 851 and 2045 atoms at a certain temperature. The data for the clusters have been calculated as averages over ten 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.

To study the evolution of single layers in the cluster, the changes of sizes for all layers in the cluster were noted during the simulation. We observed that for all cluster sizes the layers break up in turns, so the layer breaking up is always the one on top, while the ones below are more or less static. It was also observed that as the top layer started to break up the size of the layer beneath was constant while the next layers grew. This can only be explained by atoms being shoved downwards two or more layers immediately after break-up.

Figure 6. The effective activation energy as a function of the size of the cluster. The grey line shows the activation energy for the detachment of one atom from an edge (Merikoski *et al* 1997).
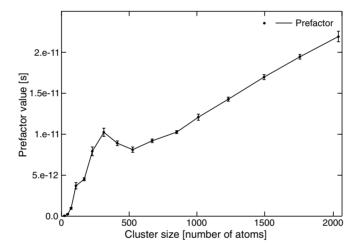

Figure 7. The prefactor as a function of the size of the cluster.

4. Discussion

Since the clusters were found to relax to a configuration of ⟨111⟩ normal surfaces in the MD simulations, the relaxation algorithm is most simply carried out by identifying the overhang positions and moving atoms from the top of the overhang to the bottom. The impact of this procedure on the time required for the cluster to be reduced to one monolayer cannot be evaluated in the KMC algorithm. However, examining the time required for this process by simulating it at different temperatures using MD showed that the relaxation process is significantly faster than the reduction process, by at least one order of magnitude, at all simulation temperatures. In figure 5 the time required for the initial relaxation is shown in comparison to the time required for the cluster to be reduced to one monolayer. As can be seen from the figure, the time required for the initial relaxation is negligible compared to the

time required for the whole reduction process for clusters consisting of less than 726 atoms. The time required for the relaxation process has a linear dependence on the cluster size; thus the time required for the relaxation of a cluster consisting of 2045 atoms will still be less than the time required for the reduction of a cluster of the same size to one monolayer. We can therefore assume that the relaxation procedure will not significantly affect the timescale of the whole reduction process.

Examining the Arrhenius behaviour for the time required for a cluster to be reduced to one monolayer more closely reveals that there are several different mechanisms involved. This can most clearly be seen by examining the fitted line and the data points in figures 4 and 5 where the data points are located below the fitted line in the high and low temperature cases. The breaking up of layers is thus a superposition of several processes whose unique balance depends on the size and shape of the cluster. The activation energy has a clear dependence on the cluster size, with a minimum for clusters of size about 100 atoms at 0.81 eV. For smaller clusters the activation energy seems to be growing strongly as the size decreases, with a maximum of 0.99 eV for a cluster with the size 22 atoms. Examining the number of processes occurring during the KMC simulations we observed that for clusters of sizes 22 and 46 atoms the number of dimer formation and dissociation processes is higher than that of surface and edge diffusion processes; hence we believe that this is the reason for the high stability of the smallest clusters. For clusters of sizes 22–107 atoms, the movement of atoms downwards by several layers from a corner is significantly more probable than for larger clusters, with a maximum at the cluster consisting of 107 atoms. This process has a activation energy of 0.66 eV and thus explains the dip in the activation energy curve (figure 6) for small clusters.

As the cluster size grows the activation energy appears to be levelling off to a value of about 0.93 eV. The closeness to 0.87 eV (determined from simulations and hard-coded in our KMC model) indicates that the main process is the atom detachment from a straight step edge (cf section 2.2). The fact that it levels off to a slightly higher value indicates that some additional process modifies the effective activation energy slightly. The main process being detachment from a straight step edge is natural since the straight edges, in the neighbourhood seen by one atom, will be very common for large clusters.

The fluxes used in experiments (Haberland *et al* 1992) for cluster deposition are of the order of 10^{12} cluster cm^{-2} s^{-1}. This implies that the time between clusters being deposited in the vicinity of each other would be of the order of seconds. From figures 4 and 5 we can see that as we are in a temperature regime higher than 400–500 K, depending on the cluster size, the timescale of the smoothing out of the cluster will be shorter than that of a new cluster landing in the vicinity of a previous one.

5. Conclusion

In this work we have developed an algorithm for relaxing a Cu cluster on a Cu surface, and incorporated it into a kinetic Monte Carlo program using the BKL scheme. Clusters consisting of 22–2045 atoms with the shape of pyramids were simulated at different temperatures using this kinetic Monte Carlo scheme and the time required for reducing the clusters to one monolayer on the surface was determined. From these results the effective activation energy could be calculated; it proved to have a dependence on the cluster size. The evolution of the clusters is built up by several different processes which interplay depending on the size and shape of the cluster.

The methods described in this paper would work for a wide range of epitaxial systems. In principle, the method can also be extended to heterogeneous systems as long as the KMC parameters can be obtained for the systems studied.

The result found in this work can be directly used to determine suitable nanocluster deposition fluxes in experiments and also provide a basis for further simulation work.

Acknowledgments

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