Long-term stability of Cu surface nanotips

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Abstract
Sharp nanoscale tips on the metal surfaces of electrodes enhance locally applied electric fields. Strongly enhanced electric fields trigger electron field emission and atom evaporation from the apexes of nanotips. Together, these processes may explain electric discharges in the form of small local arcs observed near metal surfaces in the presence of electric fields, even in ultra-high vacuum conditions. In the present work, we investigate the stability of nanoscale tips by means of computer simulations of surface diffusion processes on copper, the main material used in high-voltage electronics. We study the stability and lifetime of thin copper (Cu) surface nanotips at different temperatures in terms of diffusion processes. For this purpose we have developed a surface kinetic Monte Carlo (KMC) model where the jump processes are described by tabulated precalculated energy barriers. We show that tall surface features with high aspect ratios can be fairly stable at room temperature. However, the stability was found to depend strongly on the temperature: 13 nm nanotips with the major axes in the $\{110\}$ crystallographic directions were found to flatten down to half of the original height in less than 100 ns at temperatures close to the melting point, whereas no significant change in the height of these nanotips was observed after 10 $\mu$s at room temperature. Moreover, the nanotips built up along the $\{110\}$ crystallographic directions were found to be significantly more stable than those oriented in the $\{100\}$ or $\{111\}$ crystallographic directions. The proposed KMC model has been found to be well-suited for simulating atomic surface processes and was validated against molecular dynamics simulation results via the comparison of the flattening times obtained by both methods. We also note that the KMC simulations were two orders of magnitude computationally faster than the corresponding molecular dynamics calculations.

Keywords: copper, kinetic Monte Carlo, surface diffusion, nanotips

(Some figures may appear in colour only in the online journal)
The hypothesis does not satisfactorily explain the experimental observations of the formation of similar nanotips in connection to electrical breakdowns (see, for example [12]) and the field-emitting tips are mostly associated with particles of a foreign origin or metal dust [13, 14]. Unfortunately, this hypothesis does not satisfactorily explain the experimental results obtained recently at CERN [15], which confirms that the exact nature of the field-emitting nanotips still remains unknown. It is therefore of interest to use multiscale modelling to study how the surface behaves under high electric fields and, if any asperity emerges [16], what the lifetime of such an asperity is after the electric field is removed.

We develop our model for a copper (Cu) surface to match the material choice for the accelerating components of CLIC [3]. At the same time, Cu is a widely used material in many different high-voltage devices. To date, there exist many kinetic Monte Carlo (KMC) models for studying various processes on Cu surfaces, such as film growth due to deposition and surface roughening [17–24]. Atoms deposited on smooth metal surfaces tend to group together and form islands, which has been clearly observed by scanning tunnelling microscopy [25]. Adatom islands were previously the object of KMC studies, where the adatom migration energy barriers were either approximated by formulae based on bond-counting arguments [26, 27], or calculated on the fly by using self-learning algorithms [21, 28, 29]. The former method is fairly inaccurate and may only be effectively applied on relatively smooth surfaces, whereas the latter method is limited by its CPU intensity. A third method is to estimate the migration energy barriers in an unrelaxed rigid atom lattice using an interatomic potential. This method is fairly approximate since the barriers are dependent on how relaxed the atoms are in the system. The method has, however, been used to study adatom islands [23] and thin-film growth by deposition [20, 24]. A bond-counting rule has been applied in a KMC study of surface asperities [30], however, it was not validated against experiments nor any other methods.

Surface asperities with high aspect ratios, such as nanotips, have a geometry and behaviour similar to that of nanowires. The properties of the latter have also been studied intensively in both experiments and computer simulations, such as molecular dynamics (MD) and KMC. For instance, the MD simulations of Liang et al and Park et al showed that thin nanowires oriented along the ⟨100⟩ crystallographic directions may spontaneously reconstruct the shape to align the major axis of the wire along the ⟨110⟩ direction [31, 32]. Cu nanowires with diameters ~40 nm have also been seen experimentally to break the structural integrity during annealing at temperatures between 670 and 870 K, forming chains of spherical droplets [33]. This effect, known as ‘pearling instability’, was predicted earlier by KMC simulations of Ge nanowires by Müller et al [33] and was explained by a variant of the Rayleigh instability mechanism [34].

We present a newly developed atomistic KMC code, Kimocs, for simulating the evolution of metal surfaces on the atomic scale. In Kimocs, a rigid face-centred-cubic (fcc) lattice is assumed. The lattice spans the whole simulation system, including the bulk, surface and vacuum space above the surface (figure 1). At every KMC step, one atom may jump to an unoccupied first nearest neighbour (1nn) lattice site with a precalculated transition rate, in accordance with the general KMC algorithm [37–39]. Atom-jump processes are thermally
activated and their transition rates $\Gamma$ are thus given by the Arrhenius formula:

$$\Gamma = \nu \exp \left( \frac{-E_m}{k_B T} \right)$$  \hspace{1cm} (1)

where

- $\nu$ is the attempt frequency of the process
- $k_B$ is the Boltzmann constant
- $T$ is the temperature of the system
- $E_m$ is the migration energy (or activation energy) of the atom required to move from one lattice point to another.

In Kinos, all atom-jump processes are characterized by the number of the first nearest neighbour (1nn) and the second nearest neighbour (2nn) atoms in the three-dimensional space of the initial and final sites, as shown in Figure 2. We denote the number of 1nn and 2nn atoms at the initial site as $a$ and $b$, respectively, and the corresponding numbers for the final site as $c$ and $d$. Then, the migration energy of the jump process is described by four indices: $E_m(a, b, c, d)$. In the fcc lattice, the indices $a$ and $c$ are between 0 and 12, whereas the indices $b$ and $d$ are between 0 and 6. The values of $E_m(a, b, c, d)$ are precalculated and tabulated (section 3).

In Kinos, the fcc lattice, and thus the atoms, may be arranged in three different orientations, allowing for three different surfaces: {100}, {110}, and {111}. The boundary conditions may be periodic in all three directions: $x$ and $y$ (lateral directions), and $z$ (upwards). With non-periodic boundaries in the $z$ direction, the atoms that reach the upper boundary are removed, whereas the atoms in the bottom layer are assumed to belong in the bulk and are thus fixed.

Figure 2. Illustration of the characterization of an atom migration jump on a {100} surface in Kinos (between the two sites marked in red). Two atom layers are shown: the first layer (top, shown with filled circles) and the second layer (below, empty circles). The first nearest neighbour (1nn) sites are marked blue and the second nearest neighbour (2nn) sites are marked grey. Note that the migrating atom is counted as one of the 1nn atoms of the final (initially empty) site. To guide the eye, the face-centred cubic (fcc) unit cell is shown by black lines.

Table 1. The dimensions used for the simulated systems with different surfaces and the number of atomic monolayers (ML) used for the substrate. The $z$ direction is normal to the surface.

| Surface | $x$ [nm] | $y$ [nm] | $z$ [nm] | Substrate [ML] |
|---------|----------|----------|----------|----------------|
| {100}   | 7.4      | 7.4      | 14.8     | 12             |
| {110}   | 12.8     | 9.0      | 5.2      | 18             |
| {111}   | 9.0      | 5.2      | 12.8     | 30             |

Figure 3. Two different permutations of the (6, 3, 7, 3) atom-jump process.

The time increment at each KMC step is calculated according to the residence-time algorithm [38]

$$\Delta t = \frac{-\log u}{\sum_i \Gamma_i}$$ \hspace{1cm} (2)

where the sum is taken over all possible events $i$ at every simulation step and $u \in (0, 1]$ is a uniform random number.

2.2. Nudged elastic band

For calculating the atom migration energy barriers, the minimum energy path was found using the nudged elastic band (NEB) method [40, 41] with the MD code PARCAS [42–44]. The atomic systems for the initial and final states were constructed by Kinos. These systems had the dimensions presented in Table 1. The bottom-layer atoms were fixed. The initial and final states were relaxed using the conjugate gradient method. By linear interpolation between the atom positions of the initial and final states, 40 images were created. These images were used for the NEB calculation with PARCAS. Periodic boundaries in the lateral $x$ and $y$ directions along the surface were used. No temperature or pressure controls were used.

For the NEB calculations and MD simulations, we chose the interatomic potential based on the corrected effective medium (CEM) theory, developed by Stave et al. [45]. The potential describes the properties of Cu surfaces well [46]. For instance, the potential predicts the {111} surface to be the most stable with the surface energy 1.76 J m$^{-2}$, while the surface energies of {100} and {110} are 1.91 J m$^{-2}$, and 2.08 J m$^{-2}$, respectively [46]. For comparison, density functional theory (DFT) gives 1.952 J m$^{-2}$ for {111}, 2.166 J m$^{-2}$ for {100}, and 2.237 J m$^{-2}$ for the {110} surface [47]. The experimental value of the surface energy for the {111} surface was reported to be $\sim$1.8 J m$^{-2}$ [48, 49]. As can be seen, the...
surface energies given by the CEM potential are in good agreement with both DFT calculations and experiments.

2.3. Molecular dynamics simulations

We have also performed benchmarking MD simulations by using the PARCAS code [42–44] with neither pressure nor temperature control. The dimensions of the simulation cells and the number of atoms were selected to match the ones used in Kimocs. Periodic boundary conditions were used in the x and y directions, but not in the z direction. The bottom-layer atoms were fixed. The CEM potential for Cu [45], which was used to calculate the barriers, was also used in the MD simulations. The simulations were performed with the time step 4.06 fs until the surface nanotip had flattened down to half of its initial height, that is, the simulations stopped when no atoms were above a certain z coordinate.

3. Parameterization of the KMC model

The parameterization of the Cu material, which we used for our model, can be summarized as follows:

- The migration energy barriers are calculated using the NEB method;
- Processes involving atoms in unstable initial and/or final positions are treated separately. These positions may only appear due to the adopted rigid lattice approach and are usually part of multiple transitions;
- The attempt frequency $\nu$ is estimated from a fit corresponding to MD data.

These points will be described in detail in the following three subsections.

3.1. Migration barrier calculations

The evolution of the simulated system in Kimocs is driven by diffusion jumps of atoms from occupied (initial) sites to unoccupied (final) ones in the 1nn vicinity of the former. Each jump in the system is associated with an energy barrier, $E_m(a, b, c, d)$, where $a, b, c,$ and $d$ are the number of 1nn and 2nn atoms in the initial and final states (for details, see section 2.1). The values of $E_m(a, b, c, d)$ are calculated using the NEB method implemented within the MD code PARCAS [42–44]. The intrinsic feature of the adopted model assigns the value $E_m(a, b, c, d)$, calculated for the randomly selected positional configuration described by the $a, b, c,$ and $d$ indices, to all processes with the same set of these values. Although these identically interpreted transitions, which differ from one another by configurational arrangement only, may have slightly different energy barriers, we currently neglect these differences for the sake of computational efficiency. An exact description of the 1nn atom jumps with all positional permutations included would require about $10^7$ barriers to be calculated. However, ignoring the permutations and classifying all the transitions only by the $(a, b, c, d)$ indices, the number of required calculations is reduced by several orders of magnitude.

We used the following algorithm to calculate the migration barriers. For representative positional permutations of a certain $(a, b, c, d)$ transition, we recorded possible situations which were probable in the atomic system of interest by running Kimocs for populations of randomly distributed adatoms on $\{100\}, \{110\}$, or $\{111\}$ Cu surfaces. We also used a bulk system with a random distribution of vacancies to characterize the processes with a high number of 1nn and 2nn atoms.

The values of the migration barriers were calculated as follows. Firstly, the initial and final states of the atomic systems for a given transition (an atom jump) were relaxed using the conjugate gradient method. After that, the minimum energy path for the jumping atom to perform the transition between the initial and final states was found using the NEB method. The energy barrier, $E_m(a, b, c, d)$, was defined as the difference between the saddle point (the potential energy maximum) of the minimum energy path and the potential energy of the initial state. These energy-barrier values were then added to the database to be used in Kimocs for the actual simulations.
Table 3. Flattening of cuboid nanotips, 12 ML high with 576 atoms, on different surfaces at 1000 K; comparing MD and KMC. The simulations were stopped when the nanotips had flattened below half their original height (6 ML).

| Surface | MD [ns] | KMC [ns] |
|---------|---------|----------|
| {110}   | 9.29 ± 1.44 | 9.25 ± 1.10 |
| {111}   | 6.01 ± 1.48  | 18.8 ± 0.96  |
| {100}   | 1.62 ± 0.60  | 31.0 ± 6.61  |

We estimated the uncertainty of the barrier values obtained by using the proposed \((a, b, c, d)\) characterization. We calculated the energy barriers for different jump processes identified with the same \((a, b, c, d)\) values, as is the case of, for example, the processes shown in figure 3. On average, five different permutations were calculated for 196 different \((a, b, c, d)\) transitions on a perfect \{100\} surface with randomly distributed adatoms. The average standard deviation of the energy barriers for these 196 configurations was found to be \(0.13\, \text{eV}\) or \(14.8\%\), which gives an indication of the precision of our energy-barrier characterization and subsequently of our KMC model in general.

In some NEB relaxation simulations, atoms may diverge from the intended transition. In this kind of situation, the obtained value of the energy barrier would not correspond to the \((a, b, c, d)\) transition sought, but to another process which is described by the \((a, b, c, d)\) indices corresponding to the states where the jumping atom found itself after the relaxations. During the calculations we also encountered situations in which the atoms were relaxing into different final positions from the expected ones. In these situations, we ignored the exact position while calculating the barriers since only the values of the potential energies in the saddle point and the states where the jumping atom found itself after the relaxations are important. Since the atom relaxed into a different final state in the NEB calculations, it may be rather unphysical to force this atom into a position that is energetically unstable. This, however, will be taken into account during the next KMC step as the barrier to the stable position will have a near-zero value (section 3.2), which can be interpreted as a spontaneous transition.

In principle, the small nanosize surface features must be studied by taking into consideration the finite size effect due to the large surface areas with respect to the atoms in the bulk of the nanotips, which may dramatically affect the material properties. For instance, the melting point of thin nanowires has been shown to drop rapidly when the diameter of nanowire is below \(20\, \text{nm}\) [50]. In the same study, it was shown that 1 nm-thick nanowires may melt at room temperature. Although this process is well-captured by the used CEM potential, this effect is currently not introduced in our model. The problem with unstable neighbour atoms was accentuated for migration barrier calculations on small nanotips, as the whole structure was much less stable during the relaxation process. Therefore, more robust systems such as plane surfaces or voids in the bulk, were preferred for the barrier calculations.

### 3.2. Transitions involving atoms in unstable positions

We noticed that atoms with no more than three nearest neighbours \((a \leq 3)\) have near-zero migration barriers to perform jumps to any vacant 1nn lattice position. These processes take place instantaneously and are thus spontaneous. In the terminology of Kimocs, these atoms are said to be in unstable positions. To avoid the zero barrier problem, we apply a very small migration energy barrier to imitate the spontaneous jumps of unstable atoms:

\[
E_m(a, b, c, d) = a + b(a + c + d) + c^2 + d^2 + \frac{c}{d} \quad (3)
\]

where \(a \leq 3, c > 0,\) and \(d > 0\). For processes with \(d = 0, E_m = 10^{-4}d^{-1}\) is used. \(c > 1\) is always true, since we count the jumping atom as 1nn of the final site. Although the differences are not expected to be large, this formula gives priority to unstable atoms with less neighbours to jump before the unstable atoms with more neighbours. We assume that an atom jump to a position with a higher number of neighbours is more favourable: higher \(a\) and \(b\) thus raise the barrier, whereas higher \(c\) and \(d\) lowers it. We also take into account that 1nn atoms contribute more strongly to the value of migration barriers compared to 2nn atoms by setting the corresponding contributions \(c = 10^{-3}\, \text{eV}\) and \(d = 10^{-4}\, \text{eV}\) for the 1nn and 2nn atoms, respectively, in order to obtain the right trend. Using these parameters, the maximum migration energy for an unstable atom is \(E_m(3, 6, 1, 1) = 0.0047\, \text{eV}\), which is insignificant compared to even thermal energies \((>0.025\, \text{eV})\). This is why the processes described by these barriers will appear spontaneous in the simulations. The low-energy barriers ensure that the time increments, calculated by (2), are not overestimated.

### 3.3. The attempt frequency

Another important parameter for KMC simulations is the attempt frequency \(\nu\) required for a jump to happen (1). This parameter affects the time predicted for a studied process to be completed. Since all processes in our model are jumps by atoms to 1nn lattice sites, the attempt frequencies can be reasonably assumed to be approximately the same for all transitions. They are also frequently assumed to be of the same order of magnitude as the Debye frequency for \(\text{Cu}, \nu = 4.5 \cdot 10^13\, \text{s}^{-1}\) [51-55]. In our model we fitted the value \(\nu\) to the MD simulations (for simulation details, see section 2.3), comparing the flattening time of a surface nanotip obtained by both methods. The fitting procedure can be described as follows.

A small cuboid nanotip with 576 atoms and a height of 12 monolayers (ML) was placed on three different Cu surfaces: \{110\}, \{111\}, and \{100\}, respectively. The system dimensions are listed in table 2. Periodic boundaries were used in the lateral \(x\) and \(y\) directions. The bottom layer of atoms was fixed and monitored throughout the simulations so as not to interact with the jumping atoms of the surface. The time taken for the cuboid nanotip to flatten down in height from 12 to 6 ML at 1000 K with different attempt frequencies was recorded. The statistical uncertainty was taken into account by using ten different seed numbers for every value.
of the attempt frequency. The obtained flattening times are plotted in figure 4. The KMC values for the flattening time $t_f$ can be fitted by the function

$$t_f = \nu^{-1} \exp(c)$$

(4)

where the constant $c$ can be interpreted as $c = E_m/(k_B T)$, where $E_m$ is the average atom migration barrier at the temperature $T$ and $k_B$ is the Boltzmann constant. Here, $E_m$ is 1.156 eV for [110], 1.216 eV for [111], and 1.256 eV for the [100] case, respectively. These values do, indeed, correspond well to the barriers used in our KMC model. Comparison with the MD values (the tabulated values and discussions can be found in section 4.1.1), gives the attempt frequency values $\nu$ for the different surfaces as $7 \cdot 10^{13}$ s$^{-1}$ ([110]), $2 \cdot 10^{14}$ s$^{-1}$ ([111]), and $1 \cdot 10^{13}$ s$^{-1}$ ([100]), respectively. We chose $\nu = 7 \cdot 10^{13}$ s$^{-1}$, as it is closest to the Debye frequency value of Cu.

4. Results

4.1. Validation of the model

4.1.1. Flattening time of a nanotip on different surfaces.

Using the parameterization described in section 3, we carried out a series of Kimocs simulations to validate our model against the corresponding MD results. At first, we analysed the flattening process of 12 ML high cuboid surface nanotips with respect to the crystallographic orientation of the surface. The details of the simulation setups are the same as in section 3.3. The temperature was set to 1000 K and the simulations were stopped when the height of the cuboid nanotips had decreased to 6 ML (half of their original size).

The simulations were repeated with ten different seeds and the average flattening time was recorded for each surface, as seen in figure 6. In order to validate the KMC model, the results have been compared with MD simulations, as also shown in table 3 and figure 5. The results of our KMC simulations agree with the MD results. We also note that the KMC simulations were two orders of magnitude faster computationally than the MD simulations.

The results presented in table 3 show a very good agreement between the results obtained with KMC and MD for the nanotips built on a [110] surface as they are the most stable ones. The nanotips built on the [111] and on [100] surfaces were worse in comparison, which can be explained by the shape transformations of small-scale (diameter $\sim$2 nm) nanotips. These transformations are seen in MD simulations [31, 32], but are not accessible by KMC due to the assumed rigid lattice of the simulated material. However, overall the agreement is fairly good and does not exceed factor 20, taking into account the different nature of the two simulation techniques (no relaxation of the lattice is taken into account in KMC; also the barriers for those other than the [111] surfaces can be overestimated by NEB).

4.1.2. Thermal behaviour of surface nanotips. Analysis of the flattening time over the range of temperatures will enable the prediction of the stability of the small-sized nanotips at much lower temperatures (room and below), which are difficult to access even by KMC methods. For this, we repeated the same KMC simulations as in section 4.1.1 with temperatures ranging from 500 to 1200 K. For comparison, MD simulations of the same systems were performed only for a higher temperature range of 850 K to 1200 K. The KMC data points from 900 K and higher were averaged over 10 runs per temperature, whereas the data points for lower temperatures were performed only once. The simulations were stopped when the cuboid had been flattened down to below half its original height (6 ML). The flattening time $t_f$
was found to follow Arrhenius-like behaviour:

$$t_f = t_0 \exp\left(\frac{E_a}{k_B T}\right)$$

(5)

where the prefactor is $t_0 = 2.34 \cdot 10^{-12}$ s, the activation energy is $E_a = 0.72$ eV, and $k_B$ is the Boltzmann constant. These can be compared to the values fitted to the MD data: $t_0 = 7.33 \cdot 10^{-14}$ s and $E_a = 1.00$ eV. Both sets of $t_0$ and $E_a$ compare well to the average migration barrier and inverse of the attempt frequency of the diffusion jumps (1.04 eV and $1.4 \cdot 10^{-14}$ s, respectively). The difference may be related to the limitation of the NEB method, which predicts the most relaxed pathways for atomic transitions. In MD, some transitions with the barriers higher than predicted by NEB may naturally occur, especially at high temperatures.

The results are plotted in figure 6. At temperatures between 800 and 1100 we see a very good agreement of the KMC and MD results. The temperature dependence for the flattening time shows very similar trends for both methods, with the KMC data showing slightly weaker dependence on the temperature than that of the MD. At the low temperatures (below 850 K), comparison is not possible, since MD is too slow to produce any sensible data in this regime. The dashed line is an extrapolation obtained by fitting (5), to the MD data (filled squares).

4.1.3. Formation of adatom islands. We have also analysed the migration of single adatoms on the surface to assess whether the model can satisfactorily capture the surface diffusion on Cu surfaces. We studied the dynamics of adatom migration by randomly distributing 300 adatoms on an atomically smooth surface. Three different surfaces were considered: \{100\}, \{111\}, and \{110\}. The dimensions of the surfaces were $10 \times 10$ nm$^2$. We observed that adatom islands were formed in less than 1 ns on all three surfaces. Moreover, the bigger islands were growing at the expense of smaller ones according to the Ostwald ripening mechanism.

In figure 7 we show examples of the nanoislands formed on all three different surfaces. As can be seen, the faster diffusion process on the \{111\} surface results in clearly separated and well-defined big islands. The \{110\} surface exhibits the least pronounced structure as the preferential migration along \{110\} surface channels leads to the formation of elongated and less organized structures.
4.2.1. The flattening process of large nanotips. Tall and sharp surface nanotips with high aspect ratios are believed to be responsible for the enhanced field emissions and, subsequently, the vacuum arcs observed in experiments with high electric fields [5–7]. The exact shape of these nanotips and how they are created is not known. Tips are not likely to be seen after vacuum arc events. It is also quite difficult to observe nanotips which may have grown under an electric field, but have not yet caused a vacuum arc. No such evidence exists in the literature to our knowledge. This suggests that the lifetime of such nanotips is too short to be observed with electron microscopes or other experimental techniques. Using our KMC model, we have simulated the flattening process of large narrow nanotips that may be considered as candidates for field-emitting nanotips. By estimating the flattening time of the nanotips at different temperatures, we are able to evaluate the stability and lifetime of field-emitting nanotips.

In these simulations, a cuboid nanotip of 13 nm in height and 2 nm in width (aspect ratio ∼7) was constructed on a {110} surface. Consistent with our previous simulations, we continued the simulations of the tall nanotips until they shortened to half of their original height, 7 nm. We simulated the nanotips at different temperatures between 800 K and 1200 K. The results are shown in figure 8. We also simulated a nanotip of double height (26 nm; aspect ratio ∼14). At 1200 K, the nanotip necked at (164 ± 20) ns, which is about twice the flattening time of the 13 nm tall nanotip at the same temperature: (84.7 ± 5.5) ns.

In figure 9 we show the sequence of images (snapshots taken at 0.0 µs, 0.2 µs, 2.1 µs, and 6.3 µs of simulated time) of the flattening process for the 7 nm nanotip at 1200 K. We see that the main mechanism for flattening is the diffusion of atoms down from the sides of the nanotip to the substrate. At first, the close-packed {111} facets are formed on the nanotip sides, as shown in figure 10. This process stabilizes the nanotip as the atoms have more neighbours (bonds) within the plane, whereas the adatoms migrating on this plane have less bonds and thus migrate more easily. These facets then shrink layer by layer, as these atoms also diffuse towards the substrate. As in the case of the small nanotips in section 4.1.2, the flattening time again follows an Arrhenius-like trend (5) with a prefactor $t_0 = 1.43 \cdot 10^{-11}$ s and an activation energy of $E_a = 0.89$ eV. The value of the activation barrier is greater in this case, which is explained by the strong faceting of the

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**Figure 9.** The flattening of a 13 nm-high nanotip at 800 K at (a) $t = 0.0$, (b) after 0.2 µs, (c) after 2.1 µs, and (d) after 6.3 µs, when it was reduced to half of its original height. The atoms are coloured according to their coordination number (amount of 1nn atoms) to highlight the faceting of the nanotip. The nanotip is initially a cuboid with a {110} top surface and two {112} and {111} side surfaces (see figure 10 for a detailed view). After only 0.2 µs, the closed-packed {111} facets (yellow) are dominating and the {112} facets have disappeared. The ridges formed on the substrate surface are an artefact caused by the periodic boundary conditions.

**Figure 10.** Detailed view of the apex of the 13 nm nanotip in figure 9 at $t = 0.0$ (left) and $t = 0.2$ µs (right). The atoms are coloured according to their coordination numbers. The surface atoms become more bonded (due to the faceting) in the course of the simulation.
The taller nanotip, the more atoms are bonded in the closed-packed facets, and hence a higher migration energy is required for the atoms to break out of the faceted plane and diffuse.

At 300 K, no significant change of the nanotip was observed after 10 μs. Using (5), the flattening time at 300 K can be estimated as 3.1 h. The faceting of the substrate is an artefact of the periodic boundary condition and is not the result of the current model.

Since we have used cuboid nanotips for the model construction for simplicity, we verified the shape independence by also repeating the simulations with a cylindrical nanotip. The cylindrical nanotip had the same height, 13 nm, and number of atoms, 4800, as in the case of the cuboid nanotip. No significant difference in the flattening time was observed (figure 8).

4.2.2. The pearling instability of nanotips and infinite nanowires. During the simulations of tall nanotips on the {100} and {111} surfaces we found that they were unstable at 1000 K with our KMC model. The nanotips were 13 nm-high with a diameter of 2.6 nm. At 1000 K, the nanotip with the major axis in the {100} direction exhibited Rayleigh necking and separated from the substrate after 70 ns. After 400 ns, the detached nanotip had changed into two barely attached polygon-shaped crystals (figure 11(a)). The nanotip oriented
in the (111) direction also exhibited necking and detached from the surface after 100 ns. The remainder of the suspended (not attached to the substrate) nanotip developed regular facets, but was stable for at least another 300 ns (figure 11(b)). A larger (111) nanotip of height 32 nm and diameter 1.8 nm also necked at the surface, but the upper part of the nanotip, which also developed regular facets as the smaller nanotip did, remained stable for at least 900 ns (figure 11(c)). This kind of Rayleigh instability is similar to the ‘pearling instability’ effect that has been observed experimentally for Cu nanowires [33, 57].

We also repeated the simulations with 18 nm infinitely long cylindrical nanowires; all with a radius \( r = 1.1 \) nm. Periodic boundary conditions were applied, giving the effect of infinitely long wires. The wires were directed in the (100), (110), and (111) crystallographic directions. The same necking behaviour was observed for the (100) wires (figure 12) as for the (100) nanotip, whereas no necking was observed for the (110) and (111) wires (figure 13).

For a cylindrical wire with an initial radius \( r \), having sinusoidal perturbations resulting in Rayleigh instability, the ratios \( \lambda/r = 8.89 \) and \( d/r = 3.78 \) are expected if only surface diffusion is considered [33, 57]. Here, \( d \) is the average diameter of the final clusters and \( \lambda \) is the average distance between the clusters. The simulations results for the pearling of the wires at different temperatures ranging from 700 to 1000 K are shown in figure 14. If the diameters of the clusters are estimated as spheres with the same volume, good agreement with theory is obtained for both the \( d/r \) and \( \lambda/r \) ratios. The higher ratios of \( \lambda/r \) and \( d/r \) in figure 14 are observed if the diameter of the actual clusters obtained in the simulations are taken into account. The distances \( \lambda \) were taken between the centres of the clusters. No temperature dependence of \( d \) and \( \lambda \) is observed, in agreement with the simulation results of Müller et al [56]. However, the time taken for the wire to break into clusters does depend on the temperature, as shown in figure 15. The trend is the same as for the flattening process and can be described by (5) using the prefactor \( t_0 = 5.60 \cdot 10^{-12} \) s and the activation energy \( E_a = 0.95 \) eV.

5. Discussion

5.1. The model

The key assumptions of our model are that the surface diffusion processes can be correctly described by atom jumps to 1nn positions and that these jumping processes and the associated migration energy, \( E_m \), can be characterized solely by the number of 1nn and 2nn atoms of the initial and final positions (\( a, b, c, d \)), as described in section 2. Jumps to 2nn sites and concerted movements, where more than one atom moves at once, are not considered in the model.

The model also assumes that all atoms always belong to either the surface or the bulk; jumps to the vacuum above the surface are currently forbidden and evaporation is not considered. Even if clusters detach from the main simulation cell during the simulation, each cluster is considered by Kimocs as an independent system; there are no gravitational or other forces implemented that would move a detached cluster as a whole, as would be physically expected. Atoms in the detached cluster may only jump one at a time, as specified by the KMC algorithm.

5.2. The parameterization of Cu

The migration barriers for all jump processes were calculated using NEB, which is commonly used for finding the most energetically favourable migration path. Since our
parameterization depends on the number of neighbours of the jumping atom, the NEB calculations had to be discarded if any neighbour atoms moved during the relaxation of the system as the resulting barrier would not be calculated for the desired process any more. In particular, we found that atoms with less than four atoms in the 1nn positions are very likely to move during the relaxation (and are thus in unstable positions). A similar result was found for aluminium in [59], where atoms with less than three atoms in the 1nn positions were found to be unstable in atomistic simulations.

All atoms with less than four neighbours in the 1nn positions will have zero or near-zero energy barriers for jumps. Although, for simplicity, a single small barrier value for these jumps could have been assumed, it may lead to an undesired choice for a jump of an atom which has a very few bonds, but is still slightly stronger bonded than its neighbouring atom with even less bonds. For instance, having many atoms with few neighbours next to one another might result in an atom jumping to a more bonded position, leaving behind an atom with no nearest neighbours. This will lead to disintegration of the structure and, moreover, violate the principle of KMC. Thus the less stable atom must be given priority to perform the jump. To cope with this problem, we propose (3). It is designed to give near-zero barriers for unstable atoms, but the less bonded atoms will have even smaller barriers. This way, the integrity of the surface is ensured and the barriers given by (3) do not affect the overall dynamics of the system or the time estimation in (2).

Since we only consider atom jumps to 1nn positions, it is fairly reasonable to assume the same attempt frequency \( \nu \) for all processes. In our model we have fitted the value of \( \nu \), which resulted in the same flattening time for the surface nanotip as obtained with MD simulations (section 3.3). Slightly different flattening times are obtained for different surfaces with MD, as seen in table 3. It has been found in other MD studies that wires with a (100) orientation will easily undergo a transition to a (110) orientation [31, 32]. We note that the (100) to (110) lattice transition is not possible on a rigid lattice, as in the Kímocs model, since a large part of the nanowire lattice must change orientation in a concerted movement. Kímocs will not account for this transition, which explains the large discrepancy between the KMC flattening time for a (100) oriented nanotip and the MD results. For the fitting of \( \nu \), the (110) and (111) systems are thus the most reliable, and \( \nu \) is found to be between \( 7 \cdot 10^{13} \, s^{-1} \) and \( 2 \cdot 10^{14} \, s^{-1} \). The chosen value of \( \nu = 7 \cdot 10^{13} \, s^{-1} \) is the nearest to the Debye frequency, \( 4.5 \cdot 10^{13} \, s^{-1} \), as often assumed in the KMC community [51–55]. This value gives an over-estimation of the flattening time with a factor 3 for the (111) nanotip and a factor 20 for the (100) nanotip (section 4.1.1, table 3), which is acceptable.

The KMC data agree well with MD results at temperatures >800 K, but the trend differs a bit. However, we do not have MD data by way of comparison for below 850 K, as the MD method becomes too slow at low temperatures. The extrapolation of the MD data indicates that the flattening time might be much longer than the 3.1 h predicted by KMC.

By considering the dynamic behaviour of the KMC simulations, we can conclude that the general evolution of the atomic system, as observed in MD simulations, is well reproduced in the case of the flattening of small nanotips (figure 5). The coalescence of adatoms into islands, as seen in experiments and other KMC models [25], is also correctly reproduced. For the {111} surface, one limitation of our model to take into account is that adatoms may not take hcp (hexagonal close-packed) positions, as discussed in [29], as the model only allows fcc positions.

5.3. The stability of large nanotips

The KMC simulations of large surface nanotips with aspect ratios of \(~7\) show that nanotips with the (110) orientation are particularly stable compared with nanotips of the (100) or (111) orientations. The last two are susceptible to ‘pearling instability’ [33, 35, 56], that is, breaking into pieces due to Rayleigh necking. In the simulations with the pearling effect, it should be noted that no gravitational nor other external forces, are taken into account; the pieces detached from the bulk remain suspended in vacuum as an entity in this KMC model.

We have confirmed that the Rayleigh instability is correctly reproduced by our model by simulating the necking of nanowires with good agreement with theory [33, 56, 57] and experiments [33]. Rayleigh instability is seen to occur for the (100) wires, but not for the (110) and (111) wires, at temperatures as low as 700 K. This is much lower than the melting temperature of Cu, even if the finite size effect, which will reduce the melting temperature of Cu nanowires with a thickness of \(1.8–2.6 \, nm\) to \(900–1000 \, K\) [50], were to be taken into account. The observed temperature independence of the Rayleigh instability is in good agreement with the results of the KMC studies in [56].

Our simulations show that there is no significant difference in the stability of a cuboid nanotip, compared to a cylindrical nanotip with the same height and number of atoms, which can be relevant for small-scale features. It should be noted that the thickness and height of the nanotip will affect the flattening time, as already seen in KMC studies of smaller Cu surface structures by Frantz et al [30]. However, according to our simulations, given a constant room temperature, nanoscale Cu nanotips with aspect ratios even as high as \(~7\) will be stable for several hours if they have a (110) orientation and only diffusion processes are considered.

6. Conclusions

We have developed a KMC model for the long-term surface evolution of Cu. The model considers atom jumps to first nearest neighbour lattice sites on a rigid lattice. The jumps are characterized by the number of first and second nearest neighbour atoms of the initial and final sites. The KMC model has been found to be well-suited for simulating atomic surface processes and was validated by comparing flattening times of Cu surface nanotips with MD results for three different surfaces.
and different temperatures. The computational speed was two orders of magnitude higher with our model than with MD.

Tips with a (110) orientation were found to be significantly more stable than those with (111) or (100) orientations. Nanowires with a (110) orientation were also found to be stable, as well as wires with the (111) orientation. However, wires with the (100) orientation were found to be susceptible to Rayleigh instability, independent of the temperature. The stability of nanotips was found to increase strongly with decreased temperature and a 13 nm-high (110) nanotip with an aspect ratio of ~7 can be expected to be stable for hours at room temperature. However, at temperatures near the melting point, such a nanotip will be reduced to half of its height in less than 100 nanoseconds. The lifetime of a field emitter in the shape of a nanotip with a large aspect ratio can, therefore, be assumed to be extremely sensitive to the temperature just by considering the surface diffusion processes alone.

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