Nanotip-formation processes in electric fields

Ville Jansson, Ekaterina Baibuz, Andreas Kyritsakis, Flyura Djurabekova
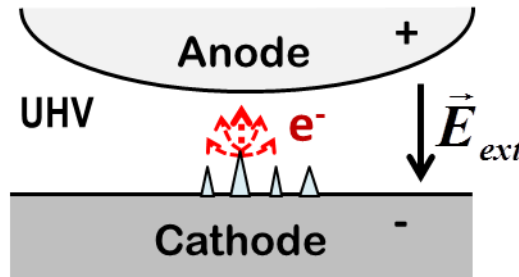**Helsinki Institute of Physics**

Sergei Vlassov, Vahur Zadin, Sven Oras, Simon Vigonski, Väino Sammelselg, Alvo Aabloo
Inst. of Technology and Inst. of Physics, University of Tartu

ville.b.c.jansson@gmail.com

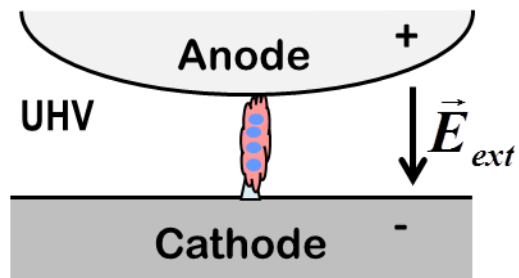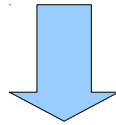**http://ville.b.c.jansson.googlepages.com**

Nanotips (cause of the arcs?)

Field-emitting tips appears and a plasma is formed

The plasma burns (breakdown) and the tips are destroyed; only craters remain

Kimocs

A Kinetic Monte Carlo (KMC) code for surfaces

- Designed to simulate the surface evolution on the atomic scale:

  - Arbitrarily rough surfaces

  - Clusters

  - Wires

  - Vacancy clusters in bulk

- Uses a rigid atomic lattice

  - fcc or bcc

- Useful for nanosecond to microsecond processes

- **Open source:**
  https://gitlab.com/vjansson/Kimocs

KMC

MD
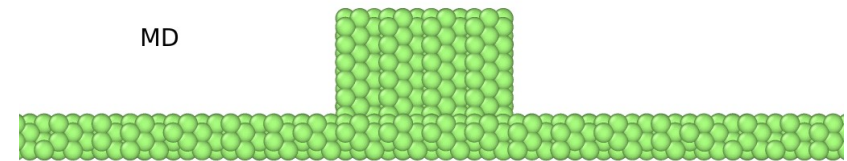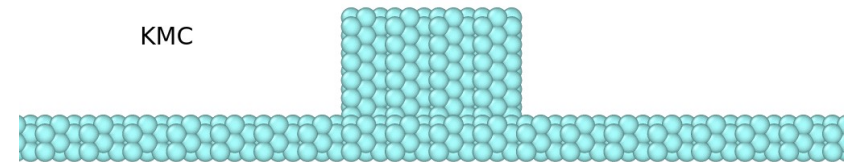
V. Jansson, E. Baibuz, F. Djurabekova (2015)

Kimocs is ~100 times faster than MD

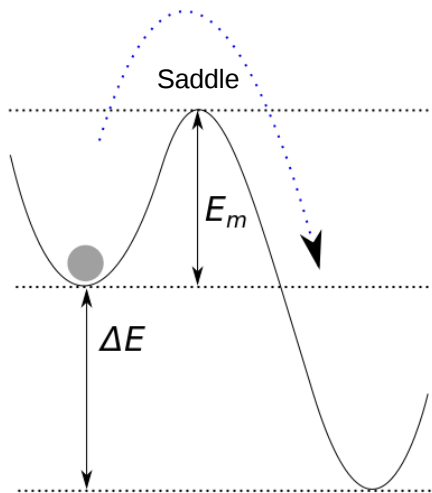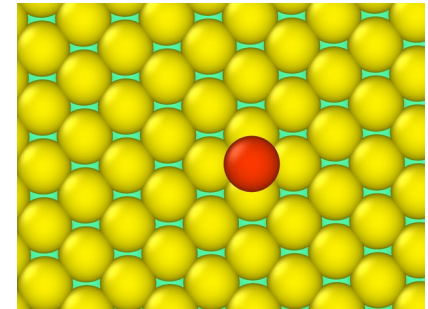V. Jansson, E. Baibuz, F. Djurabekova 2016 Nanotechnology 27 (26) 265708. http://arxiv.org/abs/1508.06870

The migration barriers

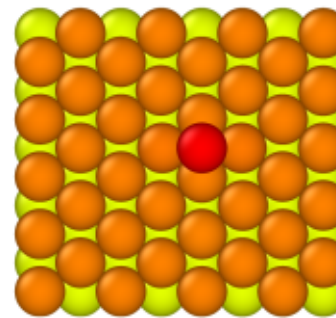Atomic jumps are thermally activated processes that happens with a frequency that is given by

$$\Gamma = \nu \exp(\frac{-B}{k_B T}),$$

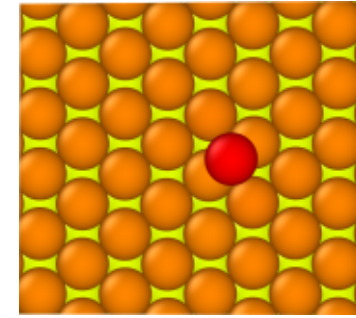where T is the temperature, ν the attempt frequency and B is the migration energy barrier.
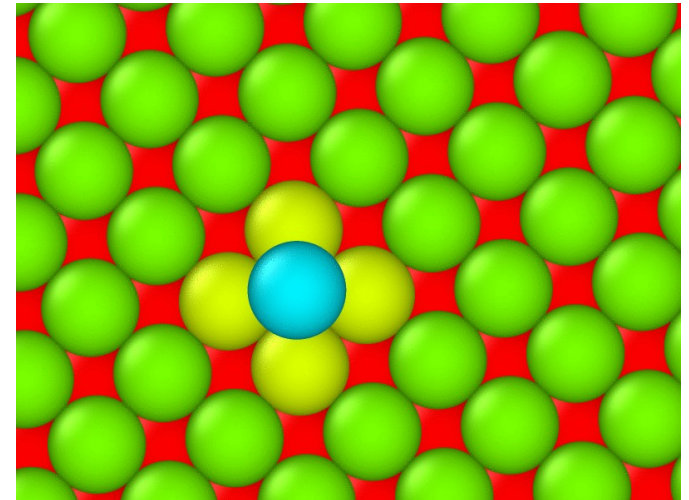

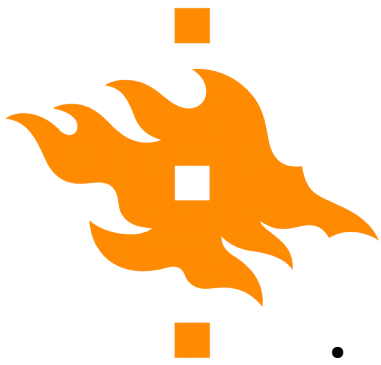
Lattice position   Saddle position

Migration barrier parameterizations

- The barriers need to be calculated with Molecular Dynamics for all possible atomic jumps, i.e. ~7000 calculations with the Kimocs parameterization

- A jump is defined by the number of nearest and second-nearest neighbour atoms of the jumping atom and the target vacancy

- This parameterization works very well with single-metal systems

Process (4,1,5,1)

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24/5/2018

Migration barrier parameterizations

- The challenge has been to efficiently calculate all barriers in MD, where e.g. the neighbour atoms or the jumping atom may relax to other than the intended positions

- This would mean the barrier is not calculated for the intended process anymore

- Our solution has been to use a small **tethering force** for all atoms in the MD calculations to make the lattice slightly more rigid

- The extra force does not significantly affect the barrier

- The great advantage is that we get a systematic and automated way to calculate barrier sets of any fcc or bcc metal (provided a good potential exist)

- Barrier sets now exist for Cu, Fe, Au, W and Ag

E. Baibuz, S. Vigonsky, J. Lahtinen, J. Zhao, V. Jansson, V. Zadin, F. Djurabkova. Migration barriers for surface diffusion on a rigid lattice: challenges and solutions, Computational Materials Science 2018, https://doi.org/10.1016/j.commatsci.2017.12.054

Migration barrier parameterizations

- If we want to include more than one element (say Cu + C), a more precise jump definition is needed where the precise position of the neigbour atoms are taken into account

- However, this means that we have $2^{26} \sim 67M$ processes to calculate (with only one element), which is not feasible

- The solution is to calculate only some of these barriers and train a Artificial Neural Network to estimate the rest (See Jyri Lahtinen's talk)
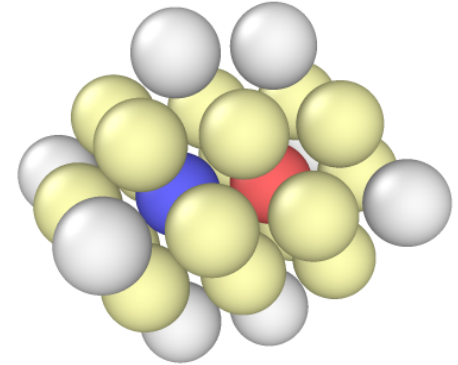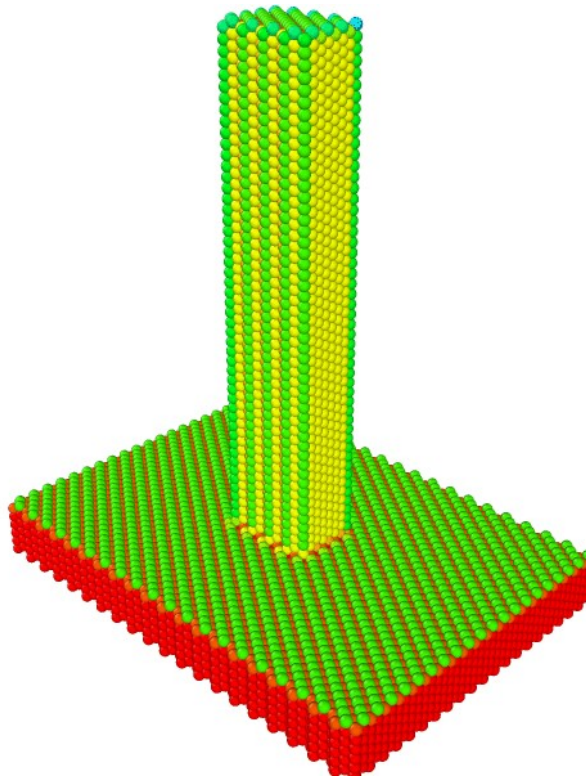
26 neigbours

J. Lahtinen, V. Jansson, S. Vigonski, E. Baibuz, Roberto Domingos, V. Zadin, F. Djurabekova. Artificial neural networks for Cu surface diffusion studies. Ready to be submitted.

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Stability of Cu nanotips

13 nm high

[110], 800 K
6.3 µs
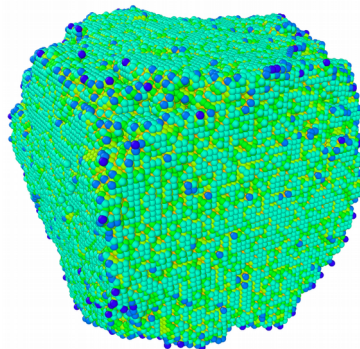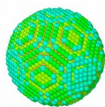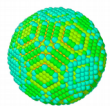
• Without field, tips flattens down
• <110> tips are the most stable ones
• At 300 K, no change was seen after 10 µs
• Extrapolation gives a flattening time of 3.1 h at 300 K

V. Jansson (2015)

BCC Fe clusters

Kimocs have been used to show how cubic Fe clusters form under deposition even though the shapes are not energetically favourable

J. Zhao, E. Baibuz et al., ACS Nano (2016)

J. Zhao, E. Baibuz et al., ACS Nano (2016)

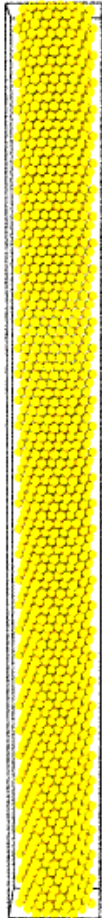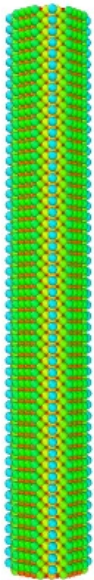J. Zhao, E. Baibuz et al., ACS Nano (2016)
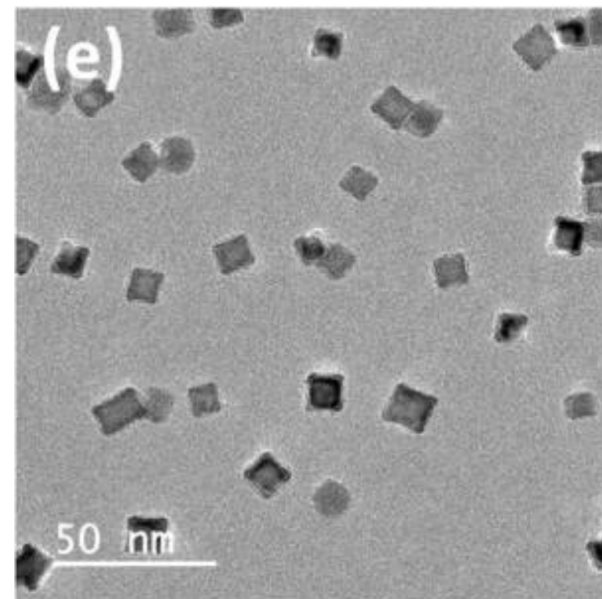
Fe clusters grown by magnetron sputtering inert gas condensation

J. Zhao et al. ACS Nano, 2016, 10 (4), pp 4684–4694
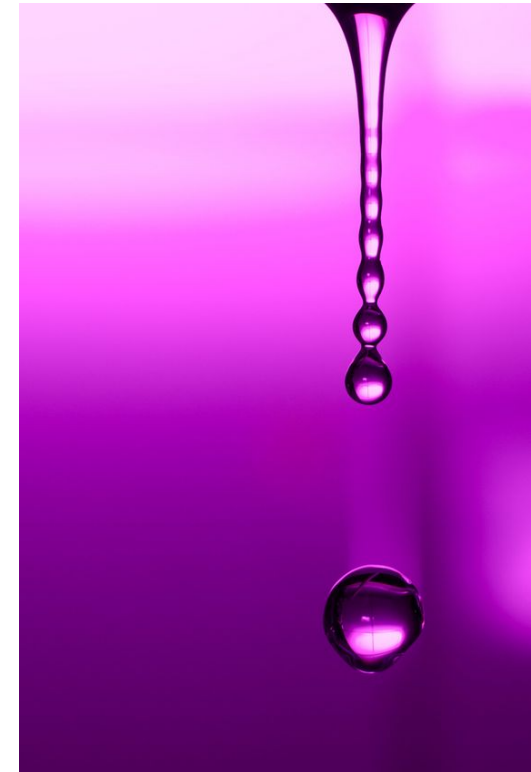
Simulations of nanowires

Cu

Au

By simulating Au crossing nanowires, we get excellent agreement with experimental observations

See talk by Simon Vigonski

Rayleigh instability

S. Vigonski, V. Jansson, S. Vlassov, B. Polyakov, E. Baibuz, S. Oras, A. Aabloo, F. Djurabekova, V. Zadin. Nanotechnology, 29(1):015704, 2018. http://arxiv.org/abs/1709.09104

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The migration barrier in electric fields

Without field, the barrier B is just the difference in the total energy of the system when the atom is at the saddle point and in the initial lattice point:

$$B_0 = E^S - E^L$$

Applying a field F meanas that the surface atoms will be polarized, which gives them some extra energy D.

A dipole is in simple terms a two charges q separated by a distance d, which gives a dipole moment $\mathbf{p} = q\mathbf{d}$.
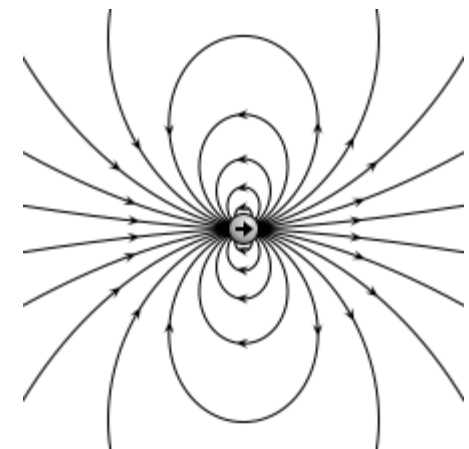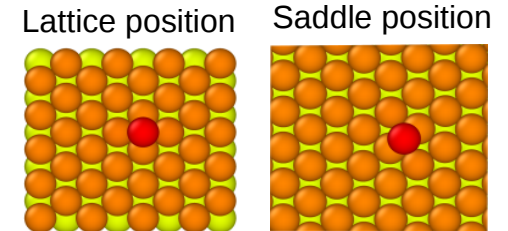
A more precise defenition, using charge densities ρ, is

$$\mathbf{p} = \int \rho(\mathbf{r})\mathbf{r}dV \approx \mu + \alpha F \dots,$$

where μ and α are called the **surface-induced (permanent) dipole moment** and **polarizability**.

The dipole energy can be expressed as

$$D(F) = -\mu F - \frac{\alpha}{2}F^2$$

Lattice position   Saddle position

Simple dipole

The migration barrier in electric fields

In my old model for the barrier in field, I used Tsong's fomula [PRB 1975] for barrier

$$B(F) = B_0 + \Delta D(\mu, \alpha, F)$$

However, when we calculated μ, α and B with DFT, we got no agreement.

We found that the dipole energy of the neighbour atoms also needed to be taken into account:

$$B(F) = B_0 + \sum_i \Delta D_i(\mu_i, \alpha_i, F)$$

ΔD is the dipole energy difference between when the adatom is in the saddle position and the lattice position. Also, μ and α will vary when the adatom is moved.

However, in DFT, the simplest is actually to define a diple moment for the whole system $p^{sys} \approx \mu^{sys} + \alpha^{sys} F$, which gives

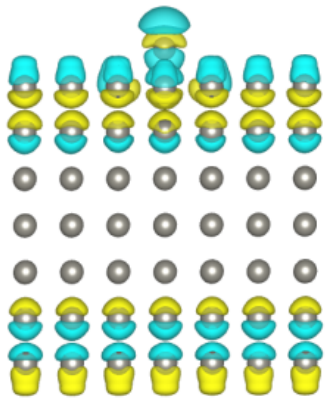$$B(F) = B_0 + \Delta D^{sys}(\mu^{sys}, \alpha^{sys}, F)$$

Atomic dipole moment
0 — 0.48
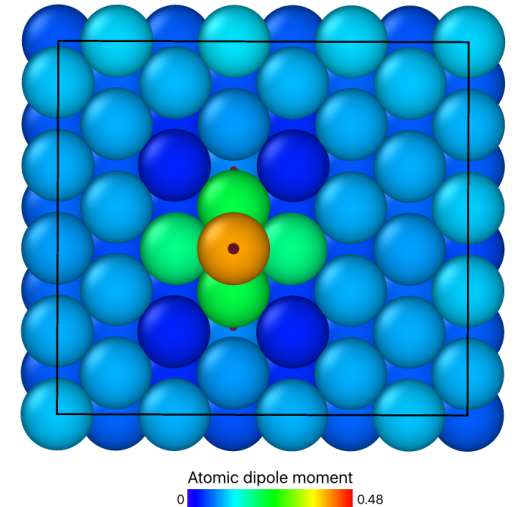
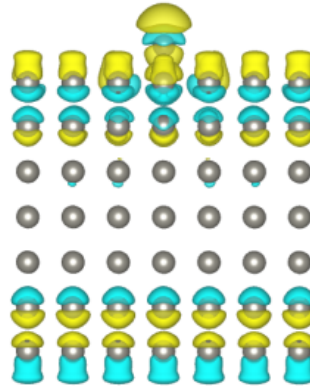E. Baibuz, A. Kyritsakis, V. Jansson, F. Djurabekova. To be submitted
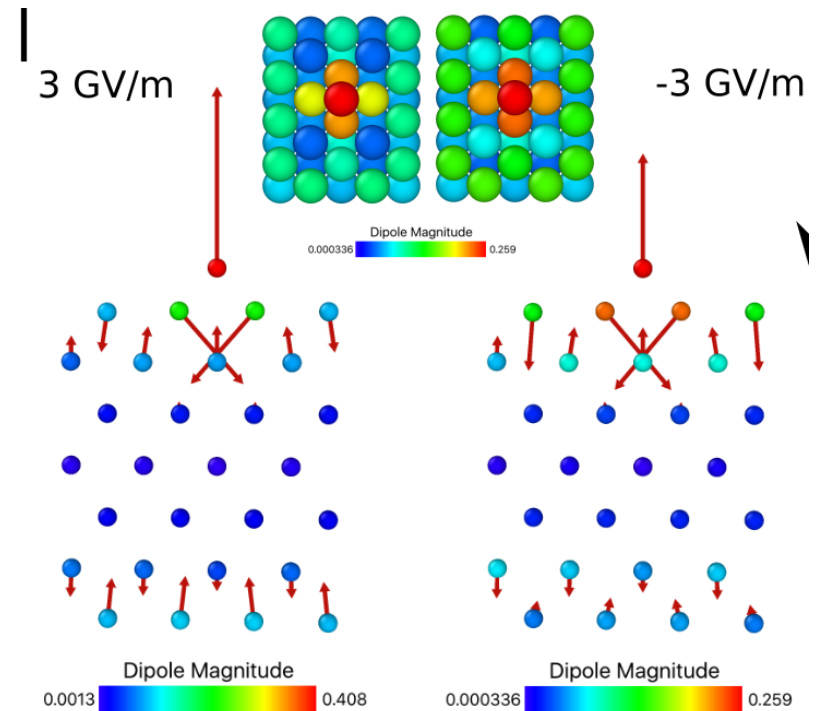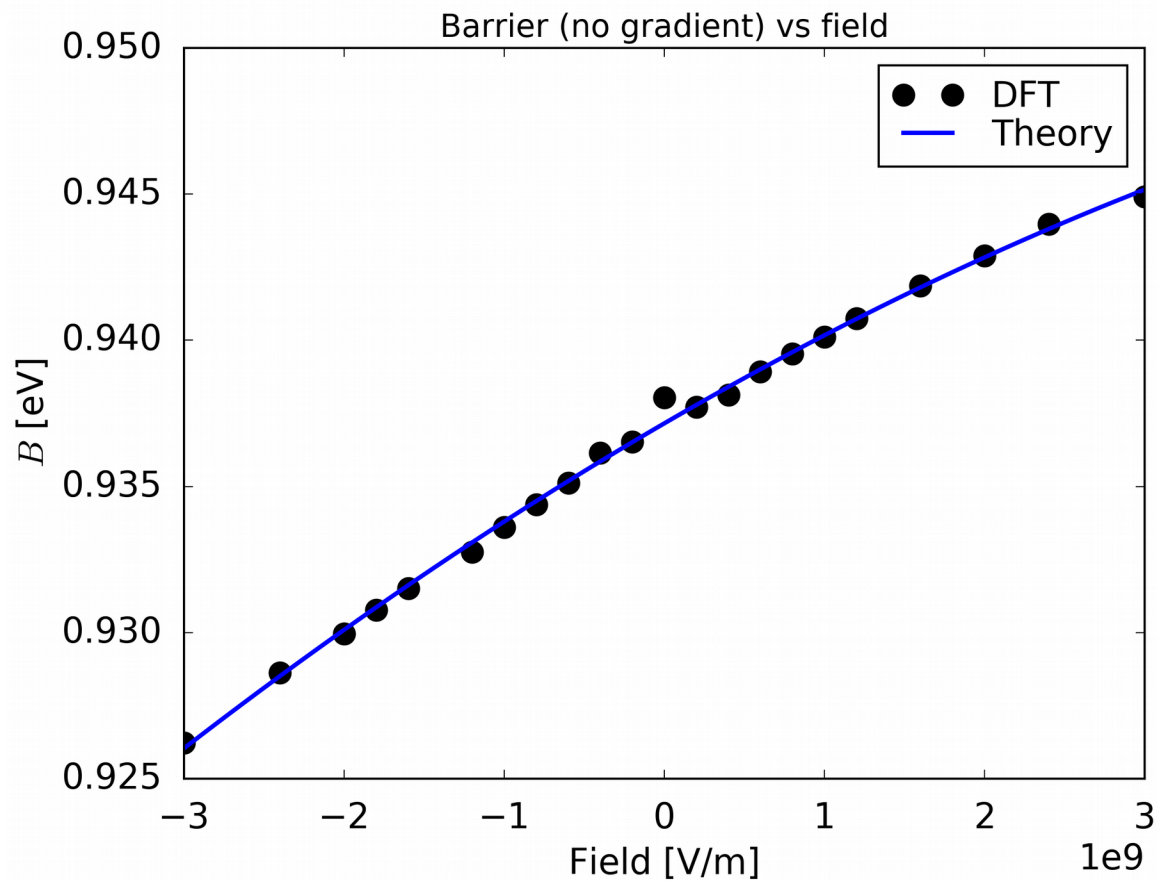
Atomic charge distribution and dipoles (DFT)

anode:

cathode:

Accumulation of electrons by electric field

Depletion

3 GV/m

-3 GV/m

Dipole Magnitude
0.000336 — 0.259

Dipole Magnitude
0.0013 — 0.408

Dipole Magnitude
0.000336 — 0.259

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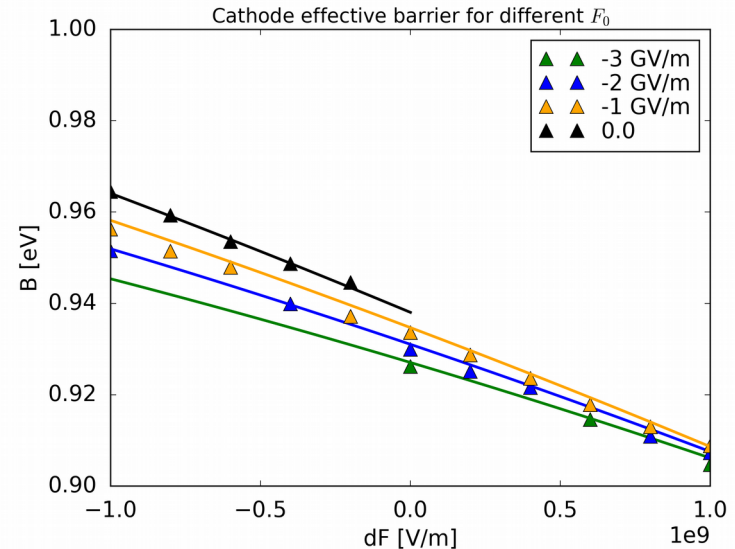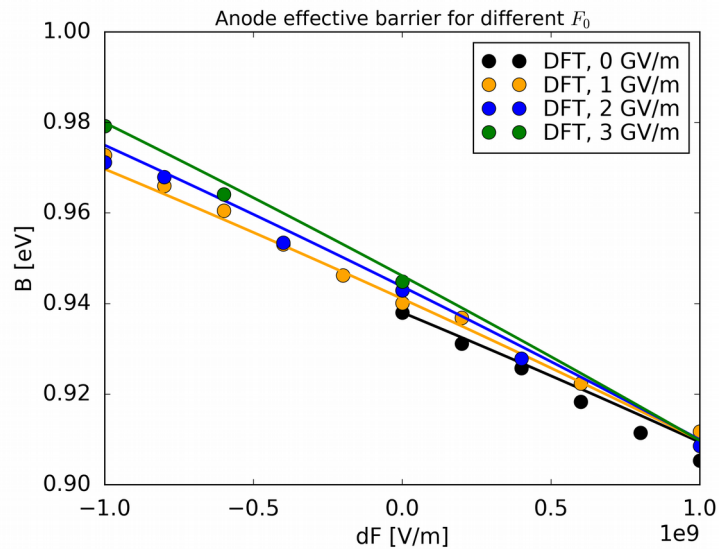
24/5/2018

Barrier with constant field: Theory vs DFT

Barrier (no gradient) vs field

Barrier with field gradient (theory vs DFT)

If we have a field gradient, the field at the saddle point will not be the same as at the lattice point. Assuming small gradients, we get the approximate formula
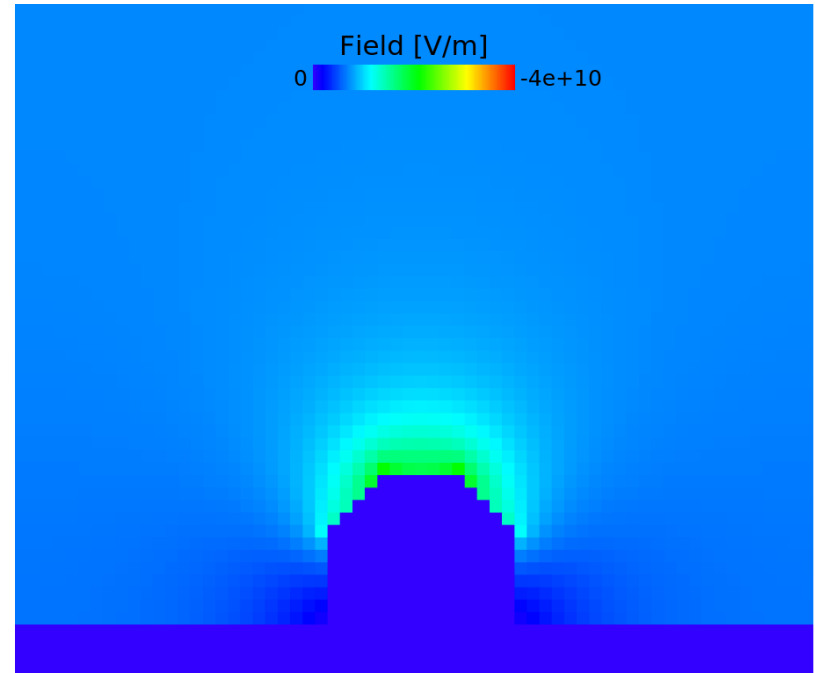
$$B(F) = B_0 + \Delta D^{sys}(\mu^{sys}, \alpha^{sys}, F) + \Delta D^{sub}(\mu^{sub}, \alpha^{sub}, F),$$

where D^{sub} is the dipole energy for the susbstrate (the system with the adatom removed).
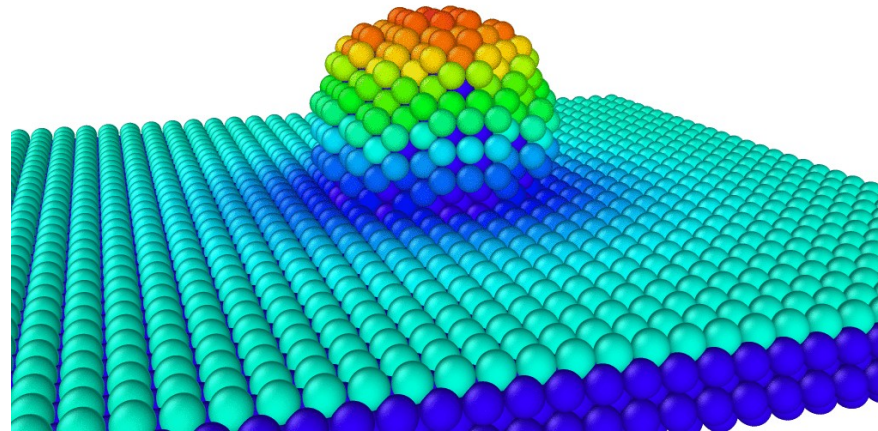
KMC + field

- Two field solvers have been implemented into Kimocs
    - HELMOD, finite difference [F. Djurabekova, PRE 2011]
    - FEMOCS, finite elements [M. Veske et al. 2018]
- The field is obtained by solving Laplace's equation

Field [V/m]
0   -4e+10

Growth of W nanotips

W nanotip at 3000 K in 10 GV/m applied field
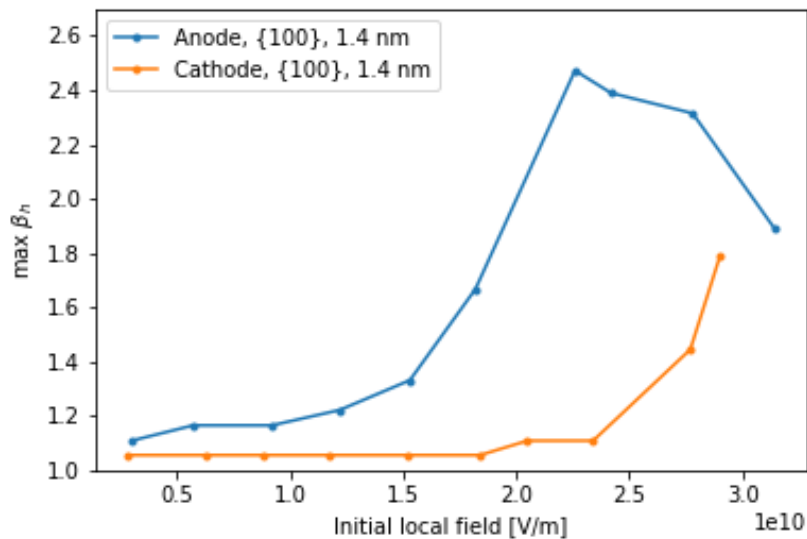

Anode

Colours: field

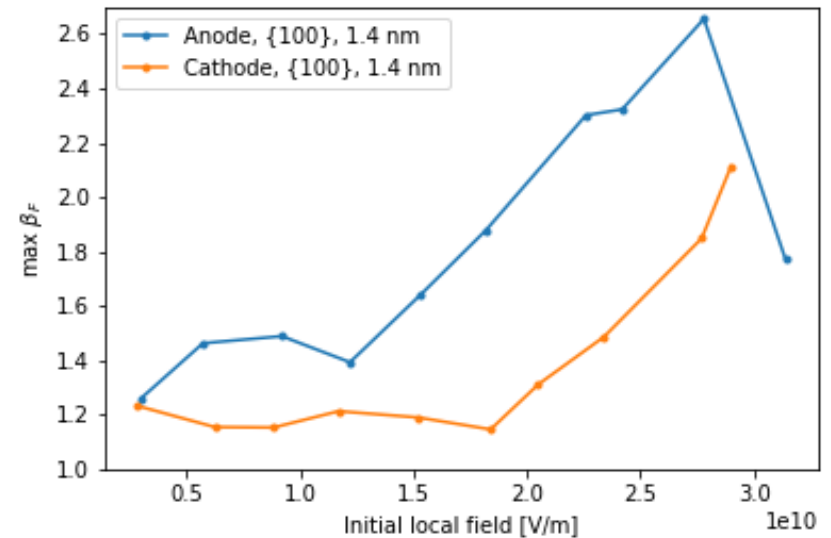The biased diffusion in fields causes formation of nanotips

Tip growth in fields

Maximum height

Maximum local field

Tip growth on both anode and cathode

Faceting of W nanotips

- Experiment by Fujita & Shioyama show faceting of W tips in fields at 2400 K
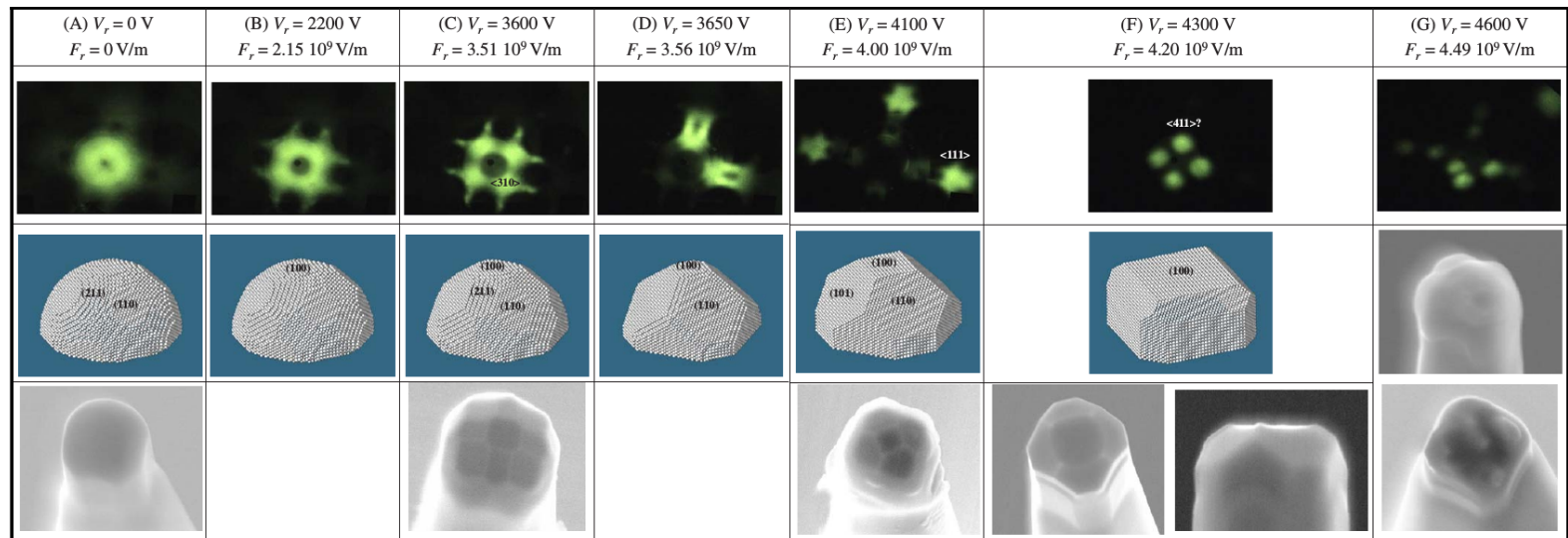- In particular a peculiar growth of a {100} facet

FIG. 5. (Color online) Summary of the evolution of the tip shape in the remolding process at the temperature $T_r = 2300$ K. The FE patterns (second row), the emitter tip shape models (third row), and the SEM images of the tips at selected stages (fourth row) are given in the order of the increasing remolding voltage.

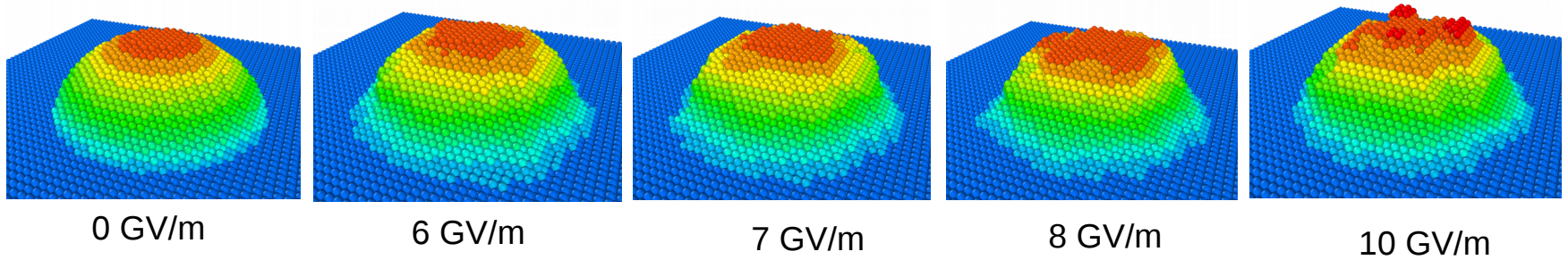S. Fujita and H. Shioyama, PRB 75, 235431 (2007)

Faceting of W nanotips

Similar growth of a W{100} facet is seen in our model
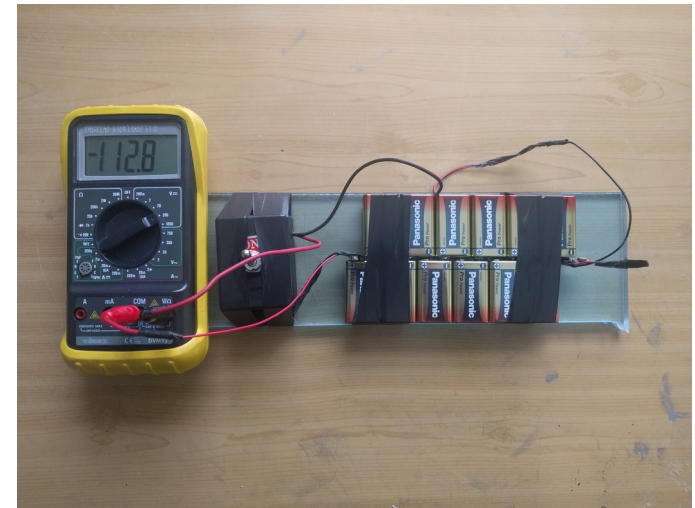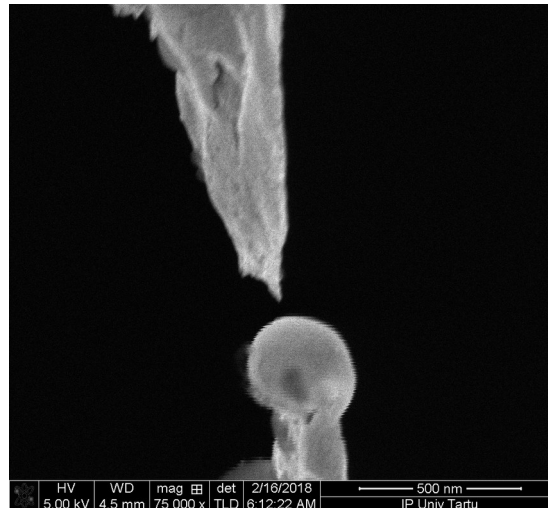

KMC

T = 2400 K

0 GV/m   6 GV/m   7 GV/m   8 GV/m   10 GV/m
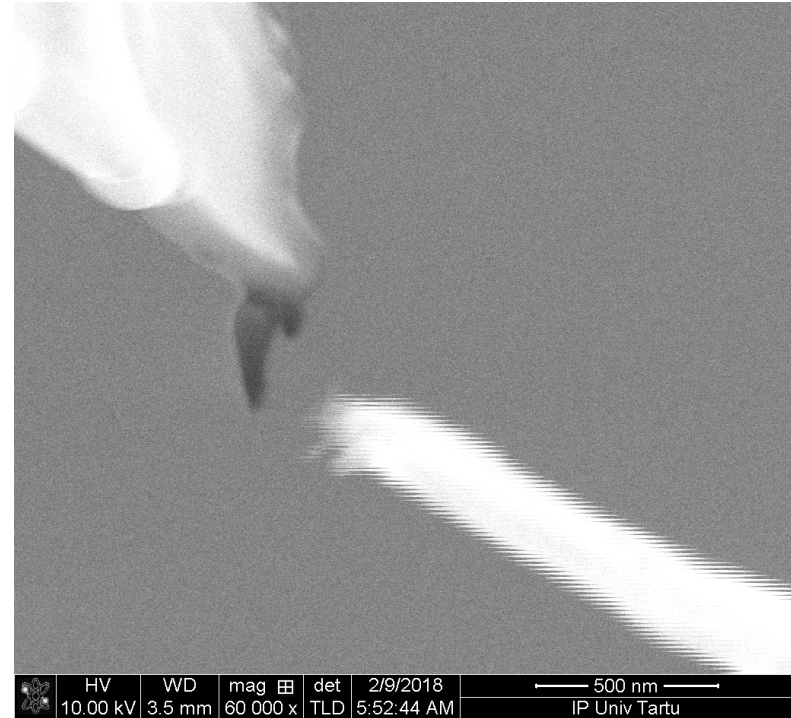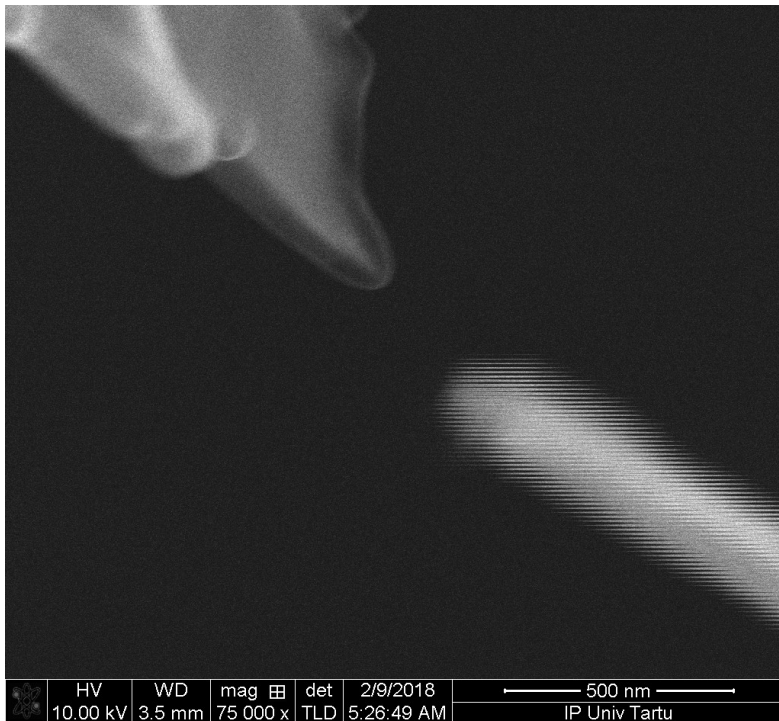
SEM investigation of Au surfaces in fields
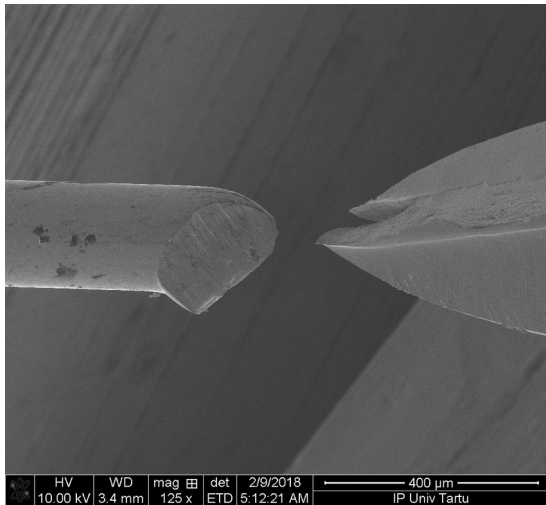
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- One static tip (left/above) and one movable tip (right/belove)

- We used Au, Pt, PtIr

- Up to 112 V applied between the tips

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S. Vlassov, V. Jansson, V. Zadin, S. Oras, S. Vigonski, V. Sammelselg, A. Aabloo

SEM results

- No Au nor Pt diffusion observed due to heavy carbon deposition and maybe too low temperatures

- However, the deposition of carbon formed a tip

| HV | WD | mag ⊞ | det | 2/9/2018 | 500 nm |
| 10.00 kV | 3.5 mm | 75 000 x | TLD | 5:26:49 AM | IP Univ Tartu |

| HV | WD | mag ⊞ | det | 2/9/2018 | 500 nm |
| 10.00 kV | 3.5 mm | 60 000 x | TLD | 5:52:44 AM | IP Univ Tartu |

S. Vlassov

Summary & conclusions

- We have a KMC code, Kimocs, that is effective enough to simulate diffusion-driven atomic surface evolution

- We have reliable barrier parameterizations for metals, such as Cu, W, Fe, Au

- We have a theory for describing the effective barriers in electric field, which is verified by DFT calculations

- The KMC model, using the field model, is able to reproduce experimentally observed faceting of W tips

- **We can be fairly certain that atomic diffusion in electric fields may grow nanotips**

  - The model predicts growth of W tips on both anode and cathode

Acknowledgement

Contact

Ville.b.c.jansson@gmail.com

http://ville.b.c.jansson.googlepages.com

Cu, 700 K