Influence of nanoscale surface modifications to the estimated field enhancement and emission currents

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MEVARC 2017
Hypotheses and Aims

• **Possible mechanism responsible of field enhancing surface modifications:**
  • material structure, fatigue and plastic deformations related causes
  • electric field assisted diffusion of surface atoms
  • reduction of work function due to the influence of oxide layers and contaminants on the surface

• **The field enhancement factor may not only be caused by high aspect ratio surface features**

• **Possible other mechanisms are**
  • dynamic, electric field or time dependent changes of surface features,
  • change of work function (due to the oxides)

• **The AIM: Fundamental understanding of processes initiating the field emitters**

• **Checking for the possibilities of surface modifications with least possible assumptions – DFT calculaitons**
Heating and emission currents

Local emission currents – connection to the experiment

- Heat equation in steady state
- Fully coupled currents and temperature
- Emission currents concentrated to the top of the tip
- Nottingham effect included in thermal modelling

Field emitters as nanowires

\[
\sigma_w = F(Kn) \cdot \sigma_{\text{free}} \\
\kappa_w = F(Kn) \cdot \kappa_{\text{free}} \\
Kn = \frac{L_{\text{free}}}{d}
\]

- Size dependence of electric and thermal conductivity
- Conductivity in nanoscale emitters is significantly decreased (more than 10x for sub-nanometer tip)
- Knudsen number to characterize nanoscale size effects
- Wiedemann-Franz law for thermal conductivity
- Optionally, temperature dependence in finite size effects
Static surface under el. field

- Field Emission Microscopy experiment
- Collaboration with Dr. Hirofumi Yanagisawa (Max-Planck Institute of Quantum Optics)
- Surface faceting and protrusion formation
- Possible mechanism for emitter formation

H. Yanagisawa, V. Zadin et al., APL Photonics 1 (2016) 091305
We can see different surface modifications leading to small $\beta$
  - Large $\beta$ is needed

Multiplication of field enhancement factors
  - Can explain observed high beta values

Incorporates surface roughness
  - $r_1/r_2<0.1$ is needed to observe significant influence

Static behavior of single emitter – sensitivity to surface roughness

Max. enhancement

Reference sim.
Influence of work function lowering on Fowler-Nordheim plot analysis

The field enhancement factor $\beta$ is usually found from the slope of FN plot $\gamma$ by

$$\beta = \frac{-b\phi^{3/2}}{\gamma}$$

The work function is usually assumed to be $\phi = 4.5$, but if the real value is different, then the estimated enhancement is

$$\beta_{\text{estim}} = \left( \frac{\phi_{\text{estim}}}{\phi_{\text{real}}} \right)^{3/2} \beta_{\text{real}}$$
Methodology

DFT calculations

- DFT VASP code
- PBE exchange-correlation functional
- Dipole correction for electric field calculation
- Bulk atoms: 5 layers of 56 atoms = 280 total
- Periodic in x and y directions, vacuum in z direction
- Simulation box is 17.9x17.7x40.0 angstroms
- Vacuum size is 30 angstroms (minus defect)
- 111 surface, with area 316.9 ang^2

Molecular Dynamics

- Polycrystal model for MD was created with Voronoi tessellation
- Each configuration ca 1 million atoms
- Simulated systems of two different grain sizes – 5 and 8 nm
- Conjugate Gradient minimization scheme to relax the initial structure
- Periodic in x, y directions
- Free surface was created by opening the z-boundary after temperature initialization and equilibration
- Allows for natural surface stress
- Mishin Cu potential used for dynamics
- LAMMPS for doing the hard work

V. Zadin, University of Tartu
Geometries

Clean Surface  Single  Planar  Extrusion 1
Extrusion 2D 1  Extrusion 2D 2  Extrusion 2D 3  Extrusion 2

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Work function decrease due to surface defects

Smooth 111 surface from literature:
Geometries – arranged by WF

- Extrusion 1: φ=4.26
- Extrusion 2: φ=4.28
- Extrusion 2D 1: φ=4.50
- Extrusion 2D 2: φ=4.42
- Extrusion 2D 3: φ=4.38
- Planar: φ=4.57
- Single: φ=4.69
- Clean Surface: φ=4.84

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Schottky-Nordheim barrier height

Analytical emission current equations assume the Schottky-Nordheim barrier:

\[ V(x) = \phi - qFx - \frac{q^2}{16\pi\varepsilon_0 x} \]

Maximum of the barrier depend on the electric field \( F \)

\[ V_{\text{max}} = \phi - \frac{q}{2} \sqrt{\frac{F}{\pi\varepsilon_0}} \]
Potential landscape for different rough surface features with DFT under electric field
- DFT calculations done for multiple electric field values (potential shown for a geometric slice)
- Complex potential landscape is formed due to the surface protrusions

- Application of Schottky-Nordheim barrier for such defects questionable
- Difficulties with surface curvature corrected barriers expected as well (GETELEC code)
- Possible solution for work function estimation based on estimation of electron tunneling probabilities
Barrier height dependence on el. field

<table>
<thead>
<tr>
<th>Geometry</th>
<th>BH</th>
<th>WF-BH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean Surface</td>
<td>4.08</td>
<td>0.76</td>
</tr>
<tr>
<td><strong>Planar</strong></td>
<td><strong>3.86</strong></td>
<td><strong>0.64</strong></td>
</tr>
<tr>
<td>Extrusion 1</td>
<td>3.52</td>
<td>0.74</td>
</tr>
<tr>
<td>Extrusion 2</td>
<td>3.51</td>
<td>0.77</td>
</tr>
<tr>
<td>Extrusion 2D 1</td>
<td>3.96</td>
<td>0.61</td>
</tr>
<tr>
<td>Extrusion 2D 2</td>
<td>3.75</td>
<td>0.67</td>
</tr>
<tr>
<td>Extrusion 2D 3</td>
<td>3.67</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Used El. field is 1 GV/m
El field influence to work function

- Changes in barrier height remain similar to the clean surface
- Difference between WF and BH used to evaluate work function changes due to field
  - Current work function estimation methodology may be too crude
- El. Field influence to the work function expected to remain small

<table>
<thead>
<tr>
<th>Geometry</th>
<th>WF</th>
<th>BH</th>
<th>(WF-BH)</th>
<th>(WF-BH)/WF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean surface</td>
<td>4.84</td>
<td>4.08</td>
<td>0.76</td>
<td>15.7%</td>
</tr>
<tr>
<td>Extrusion 2D 1</td>
<td>4.57</td>
<td>3.96</td>
<td>0.61</td>
<td>13.3%</td>
</tr>
<tr>
<td>Planar</td>
<td>4.50</td>
<td>3.86</td>
<td>0.64</td>
<td>14.2%</td>
</tr>
<tr>
<td>Extrusion 2D 2</td>
<td>4.42</td>
<td>3.75</td>
<td>0.67</td>
<td>15.2%</td>
</tr>
<tr>
<td>Extrusion 2D 3</td>
<td>4.38</td>
<td>3.67</td>
<td>0.71</td>
<td>16.2%</td>
</tr>
<tr>
<td>Extrusion 2</td>
<td>4.28</td>
<td>3.51</td>
<td>0.77</td>
<td>18.0%</td>
</tr>
<tr>
<td>Extrusion 1</td>
<td>4.26</td>
<td>3.52</td>
<td>0.74</td>
<td>17.4%</td>
</tr>
</tbody>
</table>
System energies

- General trend – system energy decreases when electric field is applied
  - Field makes surface modifications more stable
  - Surface with islands preferred over surface with adatoms
    - Good agreement with previous KMC simulations by V. Jansson
    - Effect observed in experiments as well
- Applied field lowers planar defect energy below clean surface energy
  - Surface roughening due to field energetically feasible

Energy per atom for all geometries (in $\text{meV} = 10^{-3} \text{ eV}$)

<table>
<thead>
<tr>
<th>Field (GV/m)/Geometry</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean Surface</td>
<td>0.0</td>
<td>-0.36</td>
<td>-1.45</td>
<td>-5.81</td>
</tr>
<tr>
<td>Planar</td>
<td>3.67</td>
<td>3.46</td>
<td>2.50</td>
<td>-1.69</td>
</tr>
<tr>
<td>Single</td>
<td>3.90</td>
<td>3.61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Extrusion 1</td>
<td>24.85</td>
<td>24.72</td>
<td>23.71</td>
<td>13.93</td>
</tr>
<tr>
<td>Extrusion 2</td>
<td>24.62</td>
<td>24.46</td>
<td>23.42</td>
<td>-</td>
</tr>
<tr>
<td>Extrusion 2D 1</td>
<td>0.70</td>
<td>0.46</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Extrusion 2D 2</td>
<td>5.94</td>
<td>5.72</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Extrusion 2D 3</td>
<td>12.78</td>
<td>12.56</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Polycrystalline copper surface deformations due to applied electric field

- Mechanical response of polycrystalline surfaces
- Interaction of grain boundaries with a free surface in electric field
- Electric field is modelled as a force on the surface atoms perpendicular to the surface
- Preferential surface diffusion towards the intersections of grain boundaries with the surface

- Surface atoms identified dynamically during the run by coordination analysis
- Systems generated using Voronoi tessellation
- **Green** – fcc atoms,
- **Grey** – surface and grain boundary atoms
- **Red** – stacking faults
Surface protrusion evolution
Critical stress dependence on temperature

- Necessary stress for nucleation of surface protrusions decreases linearly with temperature from 300K to 1200K
- Stress needed for nucleation of dislocation ~4 GPa
Future plans
Conclusions

- Significant work function decrease due to the surface morphology changes
  - Flat surface 4.84 eV vs. defect 4.26 eV

- Electric field leads to formation of complex potential landscape near defects, application of Schottky-Nordheim barrier complicated
  - Current work function estimation methodology may be too crude
  - Influence of electric field to the work function estimated to be small

- Spontaneous protrusion formations possible
  - From grain boundaries or extension to other disordered material defects or spots

- Future plans: In situ SEM tests with nanowires under electric field
  - Aim to observe electric field induced surface modifications
Thank You for Your attention!

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