Electrostatic theory of metal whiskers

Victor Karpov
Department of Physics and Astronomy,
University of Toledo, Toledo OH
victor.karpov@utoledo.edu

FIG. 1. Scanning electron microscope (SEM) pictures of tin (left) and zinc (right) whiskers. Courtesy of the NASA Electronic Parts and Packaging (NEPP) Program [6].

Thank you, NEPP for inspirational pictures and presentations, and for your courtesy!

Presenting a recent publication: V. G. Karpov “Electrostatic Theory of Metal Whiskers” PHYSICAL REVIEW APPLIED 1, 044001 (2014)
Disclaimer

• Some may find the explanations insufficient, and some excessive, and some both. It is often this way when looking into areas of science that are to an excessive degree unknown or ill-understood, and many unknown elements are themselves unknown. *(Steve Smith, private communication)*

• Two parts: (A) up to slide 25—introducing some underlying concepts; (B) slides 26-54 to be delivered next time, more closely whisker related.
• Several complimentary slides by the end
• Ask questions at any time
Part A
Outline

• Motivation
  – Facts as seen by a novice
  – Hypotheses as seen by a novice
• Birdseye view of the proposed
• Background: phase transformations (minimalistic overview)
  – Classical (Gibbs) nucleation theory
  – Homogeneous and inhomogeneous nucleation
  – Post-nucleation stages: growth and ripening
  – Field induced nucleation
• Charged patches on metal surfaces
• Electric field distribution near metal surfaces
• Nucleation of whiskers
• Growth of whiskers
• Whisker statistics
• Predictions and suggested mitigation strategies
• Conclusions: what is/isn’t understood, possible future work
Motivation (facts are many)

- “...there are many phenomena that produce roughly the same thing: a tin whisker.” Bill Rollins, private communication
- Lack of remedies means lack of sufficient understanding of cause and effect relations
- Correlations observed:
  - Stresses (external or internal)
  - Oxidations
  - Interfacial defects and grain boundaries
  - Contaminations
- Always with metals (semiconductor/nano whiskers are different)
- Aspect ratios unseen with other physical objects, up to 10,000
- Broad statistical distributions of parameters (randomness)
- Significant effects of additives (at least Pb) and ambient (Ag, etc.)
- Contradictory reports on electric field effects
- In spite of significant damages -- amazingly long time (60+) since observation [exceeding that for superconductivity (1911-1957)!]
Motivation (hypotheses)

- Mainstream: whiskers relieve stress (challenged: Jadhav et. al. 2009)
- External stresses (bending, squeezing)
- Internal stresses (intermetallic compounds, dislocations, etc.)
- Stress related to hydrogen embrittlement; H is omnipresent (Ashraf Jafri, 1969)
- Reaction with oxygen introducing stress; O is omnipresent (M.W. Barsoum et. al. 2004)
- Ionic contaminations; omnipresent (possibly translated into stresses; Zn, Ag, etc., esp., T. Munson, P. Solis, 2010?)
- Stress gradients (M. Sobiech et. al. 2008)
- Multiple grain boundary features and diffusion processes that may be relevant and yet generate strong informational noise
- A mystery of high aspect ratios: why wouldn’t they collapse into ‘spheres’, as other droplets do to minimize surface energy?
- What is a long range force that drives them up?
- Is their relation to metals of essence?
- What is behind their randomness?
- What does Pb do?
Outline

• Motivation
  – Facts as seen by a novice
  – Hypotheses as seen by a novice
• Birdseye view of the proposed
• Background: phase transformations (minimalistic overview)
  – Classical (Gibbs) nucleation theory
  – Homogeneous and inhomogeneous nucleation
  – Post-nucleation stages: growth and ripening
  – Field induced nucleation
• Charged patches on metal surfaces
• Electric field distribution near metal surfaces
• Nucleation of whiskers
• Growth of whiskers
• Whisker statistics
• Predictions and suggested mitigation strategies
• Conclusions: what is/isn’t understood, possible future work
Imperfect metal surfaces contain random charged patches that create significant electric fields, up to 1 MV/cm. Like charges repel producing an outward stress. Where the material is weak enough, whiskers can grow. They provide polarization electrostatic energy gain $-p*E$. 

V. G. Karpov, Phys. Rev. Appl. 1, 044001 (2014)
In addition, these electric forces are random leading to whisker statistics

$L$ is the patch size

Beyond the patch size ($r \gg L$) whiskers grow in a random field by many oppositely charged patches

- Rapid growth while either $+$ or $-$ fields dominate along the length.
- For large lengths, $+$ and $-$ fields start balancing each other.
- Whiskers *stop growing* at certain random lengths (*statistics*)
- Can resume growth after a while

V. G. Karpov, Phys. Rev. Appl. 1, 044001 (2014)
Outline

• Motivation
  – Facts as seen by a novice
  – Hypotheses as seen by a novice
• Birdseye view of the proposed
• Background: phase transformations (minimalistic overview)
  – Classical (Gibbs) nucleation theory
  – Homogeneous and heterogeneous nucleation
  – Post-nucleation stages: growth and ripening
  – Field induced nucleation
• Charged patches on metal surfaces
• Electric field distribution near metal surfaces
• Nucleation of whiskers
• Growth of whiskers
• Whisker statistics
• Predictions and suggested mitigation strategies
• Conclusions: what is/isn’t understood, possible future work
Three stages of the 1\textsuperscript{st} order phase transitions

- 1\textsuperscript{st} order refers to PT, in which changes take place for thermodynamic quantities: volume, internal energy, chemical potential, etc. (2d order refers to PT where these quantities remain, however their derivatives change, say, heat capacity, C=\(\frac{dU}{dT}\)).
- Examples: water droplets forming from vapor, steam bubbles forming in a hot water, ice crystals forming in a water, crystalline particles forming in a glassy host, etc.
- The kinetics of 1\textsuperscript{st} order PT includes three stages:
  - (1) nucleation, where particles of a new phase are formed having minimum allowed radii,
  - (2) growth, where these particles grow not yet affecting each other, and
  - (3) coalescence (aka as ripening or Ostwald ripening) where particles compete for the material, and large particles grow at the expense of smaller ones.
More general view of nucleation and growth

• **Nucleation** is the process of forming a nucleus. It is the process in which ions, atoms, or molecules arrange themselves in a pattern... *(Wikipedia)*

• Can be applied to processes where there is no new phase, but rather shape transformations: nucleation of dry spots in the process of wet film evaporation, nucleation of voids in crystals under radiation,... nucleation of whiskers as distinct patterns.

• Can be applied outside physics: nucleation of ethnic communities in NY and Chicago, nucleation of gangs..

• In all cases, a nucleus above some finite size become stable

• Most often, nuclei assume a shape with a minimum surface area (roundish) to minimize surface energy

• The process by which that nucleus evolves is called growth
Phase boundary and cluster size

Nanoscopical formation of a condensed phase according to (a) the cluster, and (b) the density-functional approach. The dashed line visualizes the phase boundary (classical approach) between the cluster and old phase.

Dependence of the work for cluster formation on the cluster size: curve 'droplet'-for water droplets in vapor at $T = 300$ K and $P/Pe = 4$; curve 'bubble' - steam bubbles in water at $T = 583$ K and $Pe/'P = 4$. Note $n >> 1$ in both cases.

D. Kaschiev, Nucleation: Basic Theory with Applications (Butterworth-Heinemann, Oxford, Amsterdam, 2000).
Classical (Gibbs) nucleation theory: energy loss due to interface, energy gain due to bulk

Nucleation time, $\tau = \tau_0 \exp \left( \frac{W}{kT} \right)$, $\tau_0 \sim 1$ ps for solids

- Spherical nuclei
- Surface vs. bulk

$A = 4\pi R^2$
$V = 4\pi R^3 / 3$

Nucleation radius $R_0$

$F = 4\pi R^2 \sigma - 4\pi R^3 \mu / 3$, $\frac{dF}{dR} = 0 \Rightarrow$

$R_0 = \frac{2\sigma}{\mu} \sim 1-3$ nm, $W = \frac{16\pi \sigma^3}{3\mu} \sim 1$-10 eV

$\sigma$ – surface energy, $\mu$ – change in the chemical potential,

Classical nucleation theory will be used in what follows

D. Kaschiev, Nucleation: Basic Theory with Applications (Butterworth-Heinemann, Oxford, Amsterdam, 2000). K. F. Kelton, in Solid State Physics, edited by H. Ehrenreich and D. Turnbull (Academic Press, Boston, 1991), Vol. 45, p. 75.
Heterogeneous Nucleation

\[ \tau = \tau_0 \exp \left( \frac{W}{kT} \right), \quad W = \frac{16\pi\sigma^3}{3\mu} \sim 1-10 \text{ eV}, \quad kT \approx 0.025 \text{ eV} \]

- Small variations in surface energy \( \sigma \) (and or \( \mu \)) will exponentially affect nucleation rate →
- Surfaces, surface imperfections will serve as efficient nucleation centers → heterogeneous nucleation
- Gibbs theory introduces the concept of nucleation and its important parameters in general
- Heterogeneous nucleation is system/defect specific; general trends limited

\textbf{In most cases, nucleation is heterogeneous}

Dependence of the work for cluster formation on the cluster size in the case stand alone droplets in vapor, for caps on a substrate, and disks on a substrate. D. Kaschiev, Nucleation: Basic Theory with Applications (Butterworth-Heinemann, Oxford, Amsterdam, 2000).

V. G. Karpov and D. W. Oxtoby, Phys. Rev. B 54, 9734 (1996); M. Castro, Phys. Rev. B 67, 035412 (2003), V. G. Karpov et. al. J. Appl. Phys. 104, 054507 (2008).
Post-nucleation stages. Growth

- Growth by accretion
- Achieved in many steps of attaching new molecules
- Described kinetically
- A compact approach can be developed through the Fokker-Planck equation

$t$ is time, $b$ is the mobility in the radii space (proportional to the diffusion coefficient or reaction rate), $F$ is the free energy.

Similar to the relation between velocity and force ($v=bF$)

[Can be amplified with heat transfer, $T$-effects on diffusion and surface tension, and other factors, as, e.g. water droplets in clouds.]

Fokker-Planck equation will be used in what follows

E. M. Lifshitz and L. P. Pitaevskii, Physical Kinetics (Elsevier, Amsterdam, Boston, 2008); V. G. Karpov, et. al. J. Appl. Phys., 109, 114507 (2011).
Post-nucleation stages. Ostwald ripening

Large particles grow at the expense of small ones.

Average radius, \( \left\langle R \right\rangle \propto t^{1/3} \)

This stage will not be analyzed in what follows for whiskers

E. M. Lifshitz and L. P. Pitaevskii, Physical Kinetics (Elsevier, Amsterdam, Boston, 2008).
V. G. Karpov, Phys. Rev. B 52, 15846 (1995).
Field Effect. Spherical Nuclei

Field decreases nucleation barrier

Previously known for fields < 10 kV/cm

Classical nucleation theory

\[ F = 4\pi R^2 \sigma - 4\pi R^3 \mu / 3 - R^3 E^2 \varepsilon / 2 \]

Physical mechanism: electrostatic polarization and dipole energy \( W = -pE \)

W. Liu, et al. J. Phys. D: Appl. Phys. 30, 3366 (1997);
C.C. Koch, et al. Material Science and Engineering, A 287, 213 (2000)
Field Induced Nucleation: Needle-shaped Particles

The same volume needle has much bigger dipole moment

\[ p_{\text{needle}} \approx p_{\text{sphere}} \left( \frac{h}{R} \right)^2 \gg p_{\text{sphere}} \]

Electrostatic energy gain \( W = -pE \) much stronger for needles

Nucleation of needle shaped nuclei will dominate

V. G. Karpov, et. al: Appl. Phys. Lett., 90, 123504 (2007); Phys. Rev. B 78, 052201 (2008); Phys. Rev. B 86, 075463 (2012)
Gigantic polarizability of a metal filament

The induced charges $\pm q$ create field to cancel $E$ inside a metal $\Rightarrow$

\[
\frac{q}{h^2} \sim E \Rightarrow q \sim Eh^2 \Rightarrow p = qh \sim h^3 E \Rightarrow
\]

\[
\alpha \sim h^3 \sim V \left( \frac{h}{d} \right)^2, \quad V = \pi d^2 h / 4 - \text{volume}
\]

\[
\left( \frac{h}{d} \right)^2 \gg 1 \text{ enhancement} \quad \text{compared to sphere.}
\]

Rigorous result: $\alpha = 2h^3 \left[ 3\ln \left( \frac{4h}{d} \right) - 7 \right]^{-1}$

Image charge effect

---

L. D. Landau, et. al., Electrodynamics of Continuous Media (Pergamon, Oxford, 1984).
R. Maltby et.al., ms. under preparation
Needle Nucleation: 2D Space (h,r)

Nucleus can evolve in \(R\) or \(h\) along the transition coordinate \(X\). Given this **extra freedom**, nucleation occurs via **lower barriers**.

Ideally, \(R=0\). Practically, minimum radius stable metal filament, \(R=\alpha R_0\), \(\alpha \sim 0.1\) – dimensionless empirical coefficient.
Spherical Vs. Needle Nuclei

Characteristic field, nucleation barrier and dimensions

| Spherical | Needle-shaped |
|-----------|---------------|
| \( E_0 = \sqrt{W_0 / R_0^3 \varepsilon} \approx 10^6 \text{ V/cm} \) | \( E_c = 2\sqrt{\alpha^3 W_0 / R_0^3 \varepsilon} \approx 10^4 \text{ V/cm} \) |
| \( W = W_0 [1 + (E/2E_0)^2]^{-2} \), \( R = R_0 [1 + (E/2E_0)^2]^{-1} \) | \( W = W_0 E_c / E \), \( h = R_0 E_c / \alpha E \gg R \), \( R = \alpha R_0, \quad \alpha \sim 0.1 \) |

\( \alpha R_0 \) is a minimum radius of a continuous metallic cylinder

V. G. Karpov, et. al: Appl. Phys. Lett., 90, 123504 (2007); Phys. Rev. B 78, 052201 (2008); Phys. Rev. B 86, 075463 (2012); M. Nardone et al, Phys. Chem. Chem. Phys., 14, 13601 (2012)
Crossover from Sphere to Needle

Crossover field

\[ E_c = 2\alpha^{3/2}E_0 \approx 10^4 \text{ V/cm} \]

- Energy gain due to smaller surface area
- Energy loss due to smaller polarizability
- Energy gain due to better polarizability
- Energy loss due to larger surface area

Needle nucleation dominates strong field region!

Verification of the field induced nucleation in the phase change memory included in the complimentary slides
Examples of conducting filaments forming in strong electric fields I

Many examples of filament formation under electric bias include both detrimental effects (shunting) and useful applications (switching in resistive memory)

K. M. Kim et. al. Nanotechnology 22, 254002(2011)

I. Valov et. al., J Solid State Electrochem, 17,365(2013)

A.Sawa, Materials Today, 11, 28 (2008)

The theory of field induced nucleation shows that it is the field (rather than bias or current) driving the filament formation
Examples of conducting filaments forming in strong electric fields II

Structures pulled up by a strong electric field on the surface of a molten metal [G. A. Mesyats, Explosive Electron Emission, URO-Press, Ekaterinberg, (1998); p.29].
Part B
Outline

• Motivation
  – Facts as seen by a novice
  – Hypotheses as seen by a novice
• Birdseye view of the proposed
• Background: phase transformations (brief reminders)
  – Classical (Gibbs) nucleation theory
  – Post-nucleation stages: growth and ripening
  – Field induced nucleation
  – Homogeneous and inhomogeneous nucleation
• Charged patches on metal surfaces
• Electric field distribution near metal surfaces
• Nucleation of whiskers
• Growth of whiskers
• Whisker statistics
• Predictions and suggested mitigation strategies
• Conclusions: what is/isn’t understood, possible future work
Imperfect metal surfaces contain random charged patches that create significant electric fields, up to 1 MV/cm.

Like charges repel producing an outward stress. Where the material is weak enough, whiskers can grow. They provide polarization electrostatic energy gain $-p*E$.

V. G. Karpov, Phys. Rev. Appl. 1, 044001 (2014)
In addition, these electric forces are random leading to whisker statistics.

Beyond the patch size \((r >> L)\) whiskers grow in a random field by many oppositely charged patches.

- Rapid growth while either \(+\) or \(-\) fields dominate along the length.
- For large lengths, \(+\) and \(-\) fields start balancing each other.
- Whiskers *stop growing* at certain random lengths (*statistics*)
- Can resume growth after a while.

Whiskers along predominantly reddish \(+\) or bluish \(-\) paths.

\(L\) is the patch size.

V. G. Karpov, Phys. Rev. Appl. 1, 044001 (2014)
Electric charges on metal surfaces (Reflections I)

- **Imperfect nonmetal surfaces have electric charges**: surface states, Tamm states, oxides and other chemical modifications, deformations, polycrystalline structure, etc.

- We want to say that **the same is true for metal surfaces**. In spite of a common intuitive belief that free electrons would level out any electric nonuniformity.

- From the charge point of view, the **difference between metals and nonmetals is purely quantitative**, in the characteristic time to level out electric nonuniformities (=Maxwell or dielectric time, $\tau_M = 4\pi\rho$ where $\rho$ is the resistivity; Gaussian system).

- Over long times, dielectric = metal. No catch: **metal surfaces can bear electric charges as well.**
Electric charges on metal surfaces (Reflections II)

- We are used to think that electric fields at metal surfaces do not exist in statics because otherwise they would force currents...
- Our physics instructors forget to tell us that it is only true for uniform metals where chemical potential is constant.
- Indeed, we know from the physics of semiconductors: zero currents does not mean constant electric potential (zero field).
- Think of p-n junctions: in equilibrium there is no currents in spite of strong built-in electric fields.
- The minimum free energy requires that it is not the electric potential $\varphi$, but rather electro-chemical potential $\Phi$ that must be constant to guarantee zero currents.

$$\Phi = \varphi + \frac{\mu}{e}, \quad \mu = \text{chemical potential, } e = \text{electron charge}$$

- In nonuniform metals,

$$\mu = \mu(\vec{r}) \Rightarrow \vec{E}(\vec{r}) = -\nabla \left[ \frac{\mu(\vec{r})}{e} \right] \neq 0$$
Models of chemical potential I

1. General

Diffusion current from high concentration region is balanced by drift current from the low concentration region:

\[-D \frac{dn}{dx} = bnE, \quad b = \text{mobility}\]

Total current = 0, \( \overrightarrow{E} \neq 0 \)

2. Deformation

Atomic potentials

\[ D = \frac{d\Delta\mu}{du} \quad - \text{deform. potential,} \]

\( u = \text{dilation} \)

\[ |D| \sim 1 \text{ eV} \]

External stress, internal stress (dislocations, other defects, intra-grain pressure, other), incommensurate phases,...
Models of chemical potential II

2. Fluctuations in chemical composition

- Alloys,
- Contamination,
- Grain boundaries vs. grains
- Cottrell atmospheres around dislocations (impurity atoms attracted to the core of a dislocation)

3. Wrong grain facets orientation

4. Oxides or other dielectric layers capable of charge accumulation

5. Direct ionic contamination (soup applications, etc.)
6. Grain boundaries that are certainly charged
7. Anything else making metals imperfect
Intermediate summary

• A common belief that metal surface cannot have local charges is wrong.
• The condition of electro neutrality is not among laws of nature. Instead, electrons distribute themselves in such a manner as to minimize the total free energy, not the total charge.
• In real metals, there are many factors leading to surface imperfections: external or internal stresses (and their related deformations), fluctuations of chemical composition, polycrystallinity, oxidation, ionic contaminations – with the same common denominator that they are conducive of surface charges accumulation.
Charge patch model
(the simplest random surface charge model)

- The surface must be neutral overall (zero electric flux): hence, combination of positively and negatively charged domains similar to a chess board, but not that ordered.
- Characterized by a single geometrical dimension $L$.
- Uncorrelated, rms value of charge density, $\sqrt{\langle (ne)^2 \rangle} = C$

Charge patches top view

$\gamma = \frac{e^2 \langle n(0)n(x) \rangle}{C}$

Correlation function

Charge variations along a line
Charge patch model
(some data and numerical estimates)

- Direct measurements, using AFM Kelvin probe, field emission, and admittance characterization:

  Electric potential variations of tenths of Volt per 1 micron in lateral directions $\Rightarrow$ 
  
  $E_\parallel \sim 1 - 10 \text{ kV/cm}$

  patch size $L \sim 10 \text{ micron}$

- Indirect estimates assuming the same order of magnitude surface charge density, $n \sim 10^{12} \text{ cm}^{-2}$ as in many dielectrics.

  $E_\perp \sim 4\pi ne \sim 1 \text{ MV/cm}$

(No dielectric breakdown due to micron small distances)

Overall, $E \sim 10^4 - 10^6 \text{ V/cm}$

J. B. Camp, et. al. J. Appl. Phys., 69, 7126 (1991). E. Bano, et. al. Appl. Phys. Lett., 65, 2723 (1994). J. Labaziewicz, et. al., Phys. Rev. Lett. 101, 180602 (2008). R. Dubessy, et. al., Phys. Rev. A 80, 031402R (2009). G. H. Low, et. al., Phys. Rev. A 84, 053425 (2011).
Electric field distribution

For large $r >> L$, # of patches seen from distance $r$, $N \sim (r/L)^2$.

Excess + or − charge felt

\[ \sigma L^2 \sqrt{N} \sim \sigma L r \]

Absolute value of field

\[ |E| \sim \frac{\sigma r L}{r^2} = \frac{\sigma L}{r} \]
Polarization in a nonuniform field

Field fluctuations do not cancel out polarization energy because the induced polarization fluctuates coherently and $p*E$ remains non-negative.

Polarization energy of a metal filament can be shown to take the form

$$F_E(h) = \frac{-1}{2[\ln(4h/d) - 1]} \int_0^h \int_0^x E(x)dx \, dx$$

Non-negative integrand
Outline

• Motivation
  – Facts as seen by a novice
  – Hypotheses as seen by a novice
• Birdseye view of the proposed
• Background: phase transformations (minimalistic overview)
  – Classical (Gibbs) nucleation theory
  – Homogeneous and inhomogeneous nucleation
  – Post-nucleation stages: growth and ripening
  – Field induced nucleation
• Charged patches on metal surfaces
• Electric field distribution near metal surfaces
• Nucleation of whiskers
• Growth of whiskers
• Whisker statistics
• Predictions and suggested mitigation strategies
• Conclusions: what is/isn’t understood, possible future work
Reminder: polarization energy

- Polarization of a metal filament makes it a dipole $\mathbf{p}=\alpha \mathbf{E}$ ($\alpha =$polarizability) with energy gain
  $$W=-\mathbf{p} \cdot \mathbf{E}=-\alpha E^2.$$

  responsible for filament development.
- It doesn’t depend on the field sign
- It is remarkably strong for the filament polarization is gigantic

Gigantic polarizability of a metal filament

$$\alpha \sim h^3 \sim V \left(\frac{h}{d}\right)^2, \quad V = \pi d^2 h / 4 \text{ - volume}$$

$\left(\frac{h}{d}\right)^2 \gg 1$ enhancement compared to sphere.

Rigorous result: $
\alpha = 2 h^3 \left[3 \ln \left(\frac{4h}{d}\right) - 7\right]^{-1}$

L. D. Landau, et. al., Electrodynamics of Continuous Media (Pergamon, Oxford, 1984).
Field induced nucleation of whiskers

\[ F = -\alpha E^2 + \sigma h \pi d = -\frac{2h^3}{3\Lambda} E^2 + \sigma h \pi d, \]

\[ \Lambda \equiv \ln \left( \frac{4h}{d} \right) - \frac{7}{3}, \quad \frac{dF}{dh} = 0 \Rightarrow \]

\[ h_0 = \sqrt{\frac{\pi \sigma \Lambda d}{E^2}}, \quad W = \frac{\pi \sigma d}{3} \sqrt{\frac{\pi \sigma \Lambda d}{E^2}}, \quad \nu \approx d^{-2} \tau_0^{-1} e^{\frac{W}{kT}} \]

**Comparing to data:**
Assuming nucleation rate \( \nu = 10^{-3} \text{ cm}^{-2} \text{s}^{-1} \) yields

\[ W = kT \ln \left( \frac{1}{d^2 \nu \tau_0} \right) \approx 2 \text{ eV}, \quad (\text{also } h \sim 10 \text{ nm}, d \sim 1 \text{ nm}) \]

**Requirements:**
Even for large \( E \sim 1 \text{ MV/cm} \), very small \( \sigma \sim 3 \text{ dyn/cm} \) needed*. However, \( E \sim 10 \text{ kV/cm} \), require abnormally low \( \sigma \sim 0.2 \text{ dyn/cm} \).**

**Inhomogeneous nucleation becomes a necessary element.**
(locally weak surface, defects, etc.)

*For metals, typical \( \sigma \sim 100-1000 \text{ dyn/cm} \): L. Vitos et. al. Surface Science *411*, 186 (1998)

** See complimentary slides
Conclusions from the model of field induced nucleation of whiskers

- Surface field favors nucleation of needle shaped metal nuclei of ~ 10 nm in height and ~ 1 nm in diameter
- Nucleation of spherical particles is less likely
- As nucleated, the needle will retain the tendency of growing with high aspect ratio that minimizes its free energy
- To describe the observed nucleation rates quantitatively, the model has to rely on inhomogeneous nucleation, i.e. existence of weak spots, typical of other nucleation processes
Growth of whiskers. Free energy

**Equation:**

\[ F_E = -c \cdot h^3, \quad c = \text{const \ when \ } h < L \]

\[ F_E = a - b \cdot h, \quad a, b = \text{const \ when \ } h >> L \]

Electrostatic theory determines the average free energy \( F \) vs whisker length \( h \),

\[ F = F_E + \pi \sigma h d \]
Growth of Whiskers. Fokker-Planck I

F-P equation describes kinetics of phenomena evolving in many small steps: diffusion, some types of recombination, particle growth...

\[ f(h, d), \text{ such that } f(h, d)dhdd \text{ is the number of whiskers with height and diameter in the intervals } (h, h + dh) \text{ and } (d, d + dd), \text{ respectively. The Fokker-Planck equation takes the form} \]

\[ \frac{\partial f}{\partial t} = -\frac{\partial s_h}{\partial h} - \frac{\partial s_d}{\partial d}. \]

Here, \( s_h \) and \( s_d \) are the components of the flux in the whisker dimensions space (s\(^{-1}\) cm\(^{-3}\)),

\[ s_h = -A_h f - B_{hd} \frac{\partial f}{\partial h} - B_{hh} \frac{\partial f}{\partial h}, \]
\[ s_d = -A_d f - B_{dh} \frac{\partial f}{\partial h} - B_{dd} \frac{\partial f}{\partial d}. \]

After all possible simplifications, F-P yields for the average quantities

\[ \frac{\partial h}{\partial t} = -b \frac{\partial F}{\partial h}, \quad \frac{\partial d}{\partial t} = -b \frac{\partial F}{\partial d}, \quad \text{with } b = \frac{B}{kT} \]

E. M. Lifshitz and L. P. Pitaevskii, Physical Kinetics (Elsevier, Amsterdam, Boston, 2008)
Growth of Whiskers. Fokker-Planck II

\[
\frac{\partial h}{\partial t} = -b \frac{\partial F}{\partial h}, \quad \frac{\partial d}{\partial t} = -b \frac{\partial F}{\partial d} \quad \text{with} \quad b = \frac{B}{kT}
\]

These equations have simple physical interpretation.

\[ \frac{\partial h}{\partial t} \quad \text{and} \quad \frac{\partial d}{\partial t} \] are velocities (of whisker length and diameter growth).

Because \( F \) is the (free) energy,

\[ -\frac{\partial F}{\partial h} \quad \text{and} \quad -\frac{\partial F}{\partial d} \] are (thermodynamic) forces along and perpendicular whisker axis,

\( b \) has the meaning of mobility linked to diffusivity \( B \) through the Einstein relation.

Overall, \((\text{velocity}) = (\text{force}) \times (\text{mobility})\), similar to, say, electrons in solids.

The diffusion coefficient \( B \) in whisker parameter space remains unknown.

For simplicity, it is assumed to be equal the tin self-diffusion, \( B = D \approx 10^{-18} cm^2 s^{-1} \).

V. G. Karpov, M. Nardone and M. Simon, J. Appl. Phys., 109, 114507-13 (2011).
Growth of Whiskers. Results

\[ h = \frac{h_0}{1 - t / t_0}, \quad t_0 \equiv \frac{3\lambda}{4bE_0^2h_0} \text{ when } h \ll L; \quad h = L \frac{t}{t_L}, \quad t_L \equiv \frac{3\lambda}{4bE_0^2L} \text{ when } h \gg L. \]

\[ d \approx \frac{h}{\sqrt{\lambda}} \] - very sensitive to FP approximations

Absolute values of dormant time \( t_0 \) and growth rate \( L/t_L \) are in the ballpark (see complimentary slides)

Figure 3. Measurement of: (a) whisker length vs. time; (b) instantaneous growth rate of whisker vs. time.

N. Jadhav, E. Buchovecky, E. Chason, and A. Bower, JOM (2010)
**Thermal radiation field**

Field $E$ due to random surface charge decaying with distance

Thermal radiation field $E_T$ independent of distance

Whisker growing horizontally when $E < E_T$

\[ I = \sigma_{SB} T^4 \]

\[ E_T = \sqrt{\frac{4\pi\sigma_{SB} T^4}{c}} \sim 5 \text{ V/cm} \]

\[ E_T \]

when $T = 300 \text{ K}$

\[ |E| \sim \frac{neL}{r} = E_T \implies r_c \sim 0.1 - 10 \text{ cm} \]

when $n \sim 10^{11} - 10^{12} \text{ cm}^{-2}$, $L \sim 0.1 - 10 \mu\text{m}$

**Prediction:** if this mechanism works, all whiskers should switch to horizontal growth at about the same distance $r_c$
Conclusions from the electrostatic model of whisker growth

- Whisker length vs. time is described on average:
  - Dormant period $t_0$
  - Subsequent constant growth rate $\frac{dh}{dt}$
- Predicts numbers. Generally consistent with experimental data.
- Agrees with the data assuming nucleation time $\tau << t_0$.
- Less reliable description of whisker diameter growth very sensitive to FP approximations; more work called upon.
- Limited to low thermal radiation ($E \sim 5 \text{ V/cm} @ \text{ room T}$).
- Long enough whiskers in the domain of thermal radiation are predicted to kink and evolve in horizontal directions.
- Growth kinetics have power dependencies on material parameters as opposed to the much stronger exponential dependencies for nucleation kinetics. Therefore, expect
  - Easier ways of killing whiskers at their nucleation stage;
  - Better predict whiskers at their growth stage.
Whisker statistics: approach

A whisker stops growing when its tip enters a region of low field, so its further polarization gain is overbalanced by the surface energy loss.

\[
F_E(h) = \frac{-1}{2} \left[ \ln \left( \frac{4h}{d} \right) - 1 \right] \int_0^h \left[ \int_0^x E(x) dx \right]^2 dx
\]

\[
F_E(h) = \frac{-1}{2\Lambda} \int_0^h \xi^2 dx, \quad \xi(x) = \int_0^x E(x) dx
\]

\(\xi^2\) is a sum of many random contributions. Based on the central limit theorem,*

\[
g(\xi^2) = \frac{1}{\sqrt{2\pi\Delta}} \exp \left[ -\frac{\left( \xi^2 - \langle \xi^2 \rangle \right)^2}{2\Delta} \right]
\]

- \(E\) is a linear functional of surface charge density \(n(r)\).
- Statistics of \(n\) \(\rightarrow\) statistics of \(E\) \(\rightarrow\) statistics of \(\xi^2\) \(\rightarrow\) statistics of \(F_E\) \(\rightarrow\) statistics of whisker lengths \(h\)

*See complimentary slides
Whisker statistics: results

\[ g(h) = \beta \frac{h}{L} \exp \left\{ -\gamma \left( \frac{h}{L} \ln \left( \frac{1 + \sqrt{1 + (h/L)^2}}{4 \sqrt{1 + (h/L)^2}} \right) \right)^2 \right\} \]

\[ \beta \text{ and } \gamma \text{ are numerical coefficients not too different from unity} \]

Log-normal provides a close fit in agreement with the data

T. Fang, M. Osterman, and M. Pecht, Microelectron. Reliab. 46, 846, (2006); L. Panashchenko, M.S. thesis, University of Maryland,(2009); D. Susan, J. Michael, R. P. Grant, B. McKenzie, and W. G.Yelton, Metall. Mater. Trans. A 44, 1485 (2013).
Conclusions: what is understood

- Why whiskers are metallic: high electric polarizability
- Why more or less perpendicular to surface: direction of the electric field lines
- Why whiskers parameters are statistically distributed: broad distribution of random electric patches
- Correlations between whiskers and versatile morphology/composition/stress/ambient factors: all producing surface electric charges
- Evolution pattern: long incubation period + constant growth rate reflects $E$-field distribution
- Numbers are predicted for the first time (?) for whiskers
Conclusions: what is not understood

- Microscopic nature of whiskers, their correlation with specific surface defects, chemical aspects (such as Pb)
- The role of whisker crystalline structure
- Whisker growth in 3D random electric field: winding and kinking.
- Possible role of surface (or grain boundary) diffusion limiting whisker growth.
- Whisker diameters: kinetics and statistics
- Interwhisker interactions limiting their concentration and affecting growth.
Conclusions: possible verifications/future work

• Whisker nucleation and growth in external electric fields (capacitor configuration or inside SEM)

• Whisker nucleation and growth under controlled contamination of metal surface with solutions of charged nanoparticles. This could pave a way to whisker self-healing if a suitable treatment is identified.

• Whisker nucleation and growth under the conditions of strong surface electric fields induced by surface plasmon polariton excitations. This could be used for controlled growth of metal nanowires of desirable parameters on metal surfaces.

• All in all the above is just a sketch of a theory, its multiple components calling upon further work
Acknowledgement

- Useful suggestions from Bill Rollins, Steve Smith, John Barnes, Andrew Kostic, and Ashraf Jafri are greatly appreciated.
- The author is grateful to D. Shvydka, A. V. Subashiev, I. V. Karpov, E. Chason, and D. Susan for useful discussions.
- The NASA Electronic Parts and Packaging (NEPP) Program is acknowledged for granting permission to use their figures.
- This work was performed under the auspices of the NSF Grant No. 1066749.
Complimentary slides

- Numerical estimates
- Long-range diffusion
- Central limit theorem
- Verifications of field induced nucleation theory for phase change memory applications
- Surface Plasmon Polaritons
- Example of self-healing electrolyte treatment in photovoltaics
Complimentary slide: numerical estimates

Surface energy. From expression for \( W \), \( \sigma \approx \left( \frac{W^2 E^2}{d^3 \Lambda} \right)^{1/3} \).

Set \( W=2 \text{ eV}=3.2 \times 10^{-12} \text{ erg} \), \( E=10^6 \text{ V/cm} \approx 3000 \text{ CGSE} \), \( d=1 \text{ nm}=10^{-7} \text{ cm} \), \( \Lambda=3 \). This yields \( \sigma \approx 3 \text{ dyn/cm} \). Assuming \( E=10^4 \text{ V/cm} \) makes it \( \sigma \approx 0.15 \text{ dyn/cm} \).

Growth kinetic parameters.

\( B = 10^{-18} \text{ cm}^2\text{s}^{-1} \), \( kT=0.025 \text{ eV}=4 \times 10^{-14} \text{ erg} \), \( b = B / kT = 2.5 \times 10^{-5} \text{ cm}^2\text{s}^{-1}\text{erg}^{-1} \).

Dormant time, \( t_0 = \frac{3\Lambda}{4bE_0^2h_0} \approx 3 \text{ years}, 300 \text{ hrs}, 3 \text{ s} \)

for respectively: \( E=10 \text{ kV/cm}, 100 \text{ kV/cm}, 1 \text{ MV/cm} \).

Growth rate \( \frac{dh}{dt} = \frac{L}{t_L} \) with \( t_L = \frac{3\Lambda}{4bE_0^2L} \) and \( L=10 \text{ \mu m}=10^{-3} \text{ cm} \):

\[ \frac{dh}{dt} = 1 \text{ A/s}, 100 \text{ A/s}, 1 \text{ \mu m/s} \] for respectively: \( E=10 \text{ kV/cm}, 100 \text{ kV/cm}, 1 \text{ MV/cm} \).
Complimentary slide: long-range diffusion

• Whiskers growing from their roots without forming surrounding dents is interpreted as a result of long range uniform drift of material towards whisker roots

• If charges are tightly pinned to the surface material, the system should maintain uniform material density to provide the minimum electrostatic energy; hence, long range drift. (according to the electrostatic theory)

• The charge drift moving the rest of material can be a result of hydrodynamic drag (to be verified yet).

• The property of flat surface and related long-range diffusion can be a separate issue (very often relevant) not necessarily related to whisker thermodynamics

T. A. Woodrow, Proceedings of SMTA International Conference, Rosemont, IL, 2006 (SMTA International, Edina, MN, 2006), pp. 1–50; E. R. Crandall, Ph.D. thesis, Auburn University, Auburn, Alabama, 2012
Complimentary slide: Central limit theorem in general

**CLT** is a purely mathematical statement that, given certain (reasonable) conditions, the sum of a sufficiently large number of random variables, each with a well-defined expected value and dispersion, will be normally distributed. *(Chebyshev, Lyapunov, Markov 1901-1935)*

…”*The huger the mob, and the greater the apparent anarchy, the more perfect is its sway.*” *(F. Galton, French mathematician)*

CLT is uniquely significant in random processes because it does not depend on the particularities of probabilistic distributions of individual terms in the sum.

See e. g. C. Kittel "Elementary statistical physics", Dover, NY, 1958, 1986
Complimentary slide:
Central limit theorem for whiskers

Need a probabilistic distribution for $\xi^2$, where $\xi(x) = \int_0^x E(x) dx$ and $E(x)$ is a random field.

Representing the integral as a sum, $\xi(x) = \int_0^x E(x) dx \approx \sum_i E(x_i) \Delta x_i$,

$$\xi^2 = \sum_{i,j} E(x_i)E(x_j)\Delta x_i\Delta x_j$$ is a sum as well.

Hence CLT applicability, $g(\xi^2) = \frac{1}{\sqrt{2\pi\Delta}} \exp \left[ -\frac{(\xi^2 - \langle \xi^2 \rangle)^2}{2\Delta} \right]$. 
This complimentary slide illustrates verifications of field induced nucleation theory; Switching Mechanism in Phase Change Memory

- Electric field lowers nucleation barrier
- Needle enhances electric field (lightning-rod behavior),
- Subsequent nucleation switches the device
Threshold voltage and switching time vs. material parameters

\[ V_{th} = \frac{V_{max}}{\ln(\tau / \tau_0)} , \quad V_{max} = 2l \frac{W_0}{kT} \sqrt{\frac{\alpha^3 W_0}{\varepsilon R_0^3}} \]

\[ \tau = \tau_0 \exp \left( \frac{W_0 \tilde{V}}{kTV} \right) , \quad \text{when} \quad V > \tilde{V} \equiv 2l \sqrt{\frac{\alpha^3 W_0}{\varepsilon R_0^3}} \]

Switching limits

(no S) \quad V < \tilde{V} \approx 0.2 \text{ V} , (S) \quad V_{max} \approx 20 \text{ V} < V \text{ (fastestS)}

V. G. Karpov, et. al; Appl. Phys. Lett., 90, 123504 (2007); Phys. Rev. B 78, 052201 (2008); Phys. Rev. B 86, 075463 (2012)
This complimentary slide illustrates verifications of field induced nucleation theory;
Verification – delay time

\[ \tau = \tau_0 \exp \left( \frac{W_0 \tilde{V}}{kT V} \right) \text{ when } V > \tilde{V} \]

V. G. Karpov, et. al: Appl. Phys. Lett., 90, 123504 (2007); Phys. Rev. B 78, 052201 (2008); Phys. Rev. B 86, 075463 (2012)
This complimentary slide illustrates verifications of field induced nucleation theory;

**Verification: temperature**

\[
V_{th} = l \sqrt{\frac{3\pi^2 \alpha^3 W}{32\varepsilon R^3}} \left( \frac{W}{kT} \right) \left[ \ln \left( \frac{t}{\tau} \right) \right]^{-1}
\]

\[V_{th, Volt} = 1.00, 1.02, 1.04, 1.06, 1.08, 1.10, 1.12, 1.14\]

Counts

\[T^{-1} (K^{-1})\]

V. G. Karpov, et. al: Appl. Phys. Lett., 90, 123504 (2007); Phys. Rev. B 78, 052201 (2008); Phys. Rev. B 86, 075463 (2012)
This complimentary slide illustrates verifications of field induced nucleation theory;

**Verification: thickness**

\[ V_{th} = A \cdot l \]

\[ V_{th} = l \sqrt{\frac{3\pi^2 \alpha^3 W}{32\varepsilon R^3}} \left( \frac{W}{kT} \right) \left[ \ln \left( \frac{t}{\tau} \right) \right]^{-1} \]

- Initially amorphous
- Programmed from crystalline

---

V. G. Karpov, et. al: Appl. Phys. Lett., 90, 123504 (2007); Phys. Rev. B 78, 052201 (2008); Phys. Rev. B 86, 075463 (2012)
Complimentary slide: Surface plasmon polariton

- Surface plasmon polaritons (SPPs), are infrared or visible electromagnetic waves, which travel along a metal-dielectric or metal-air interface. They involve both charge motion in the metal (surface plasmons) and electromagnetic waves in the air or dielectric (polaritons).

- SPPs can have tighter spatial confinement and higher local field intensity with the enhancement factors up to ~ 1000.

- Coupling of photons into SPPs can be achieved using a coupling medium such as a prism or grating to match the photon and surface plasmon wave vectors.

See e. g.: S. A. Maier, Plasmonics: Fundamentals and Applications (2007), Wikipedia, many other sources
Complimentary slide:
“Red wine” effect: self-healing

- Patching nonuniformity: act on surface, don’t worry about bulk
- Approach differs from classical crystalline PV focused on defects

Y. Roussillon et al. Appl. Phys. Lett. (2004); Patent: V. G. Karpov et al. 2006
Complimentary slide: Self-healing: examples

Self-healing alone increased CdTe PV efficiency
From 2-3% (untreated) To 10-11% (treated)

Y. Roussillon et. al. (2004)
Red wine leads UT scientists to juice up potency of solar cells

By JENNI LAIDMAN
BLADE SCIENCE WRITER

Red wine, what can beat it? It reduces your risk of heart disease. It's full of cancer-fighting compounds. And now, researchers at the University of Toledo reveal yet another use for the juice of the grape.

It makes better solar cells.

UT researcher Yann Roussillion didn't expect wine to boost the efficiency of solar cells.

Red Wine Mends Solar Cells

Technology Research News  March 19, 2004

University of Toledo researchers have found a way to increase energy productivity of red wine.

One challenge in making solar cells more efficient is countering the effects of bad spots. These spots drain current, making devices like solar cells less efficient.

The researchers have found a way to use properties of the bad spots to seal the working area of the cell. The researchers used the method to boost the efficiency of cadmium telluride/cadmium sulfide solar cell from 2 percent to 11 percent.

South America NPR interview...
Complimentary slide:
Patent granted and exclusively licensed
...sadly..

US 7,098,058 B1

12 United States Patent Karpov et al.

Patent No.: US 7,098,058 B1
Date of Patent: Aug. 29, 2006

ARTICLE 1 - DEFINITIONS

1.1 “AFFILIATE” means any corporation or other entity that is directly or indirectly controlling, controlled by, or under the common control of Corporation located at For the purpose of this Agreement, “control” means the direct or indirect ownership of at least fifty percent (50%) of the outstanding shares or other voting rights of the subject entity to elect directors, or if not meeting the preceding, any entity owned or controlled by or owning or controlling the maximum control or ownership right permitted in the country where such entity exists.

1.2 “FIELD” means cadmium telluride solar modules.