# Surface Diffusion in Glasses: Metallic/Organic

J.H. Perepezko

University of Wisconsin-Madison

Department of Materials Science and Engineering

perepezk@engr.wisc.edu

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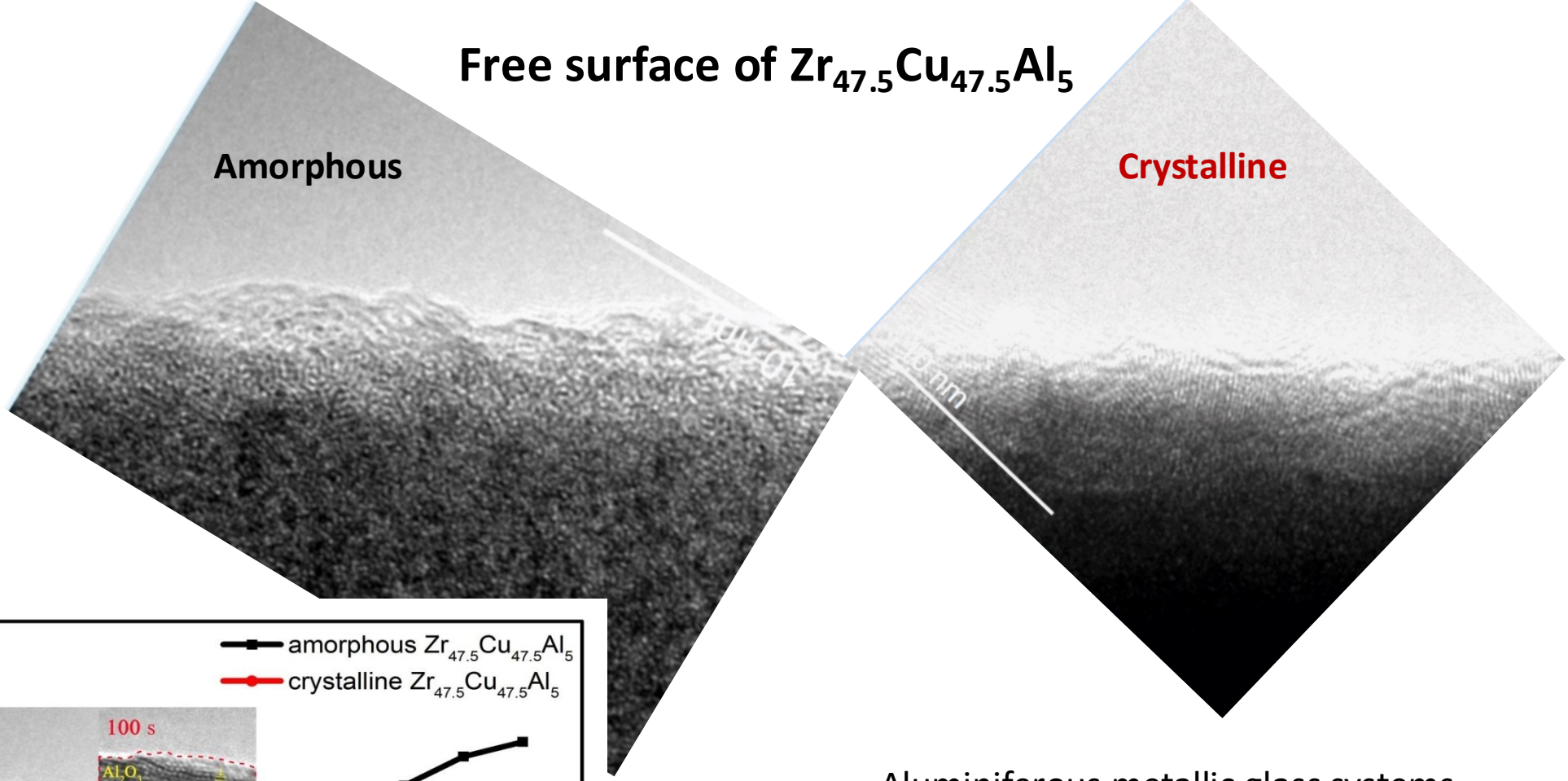
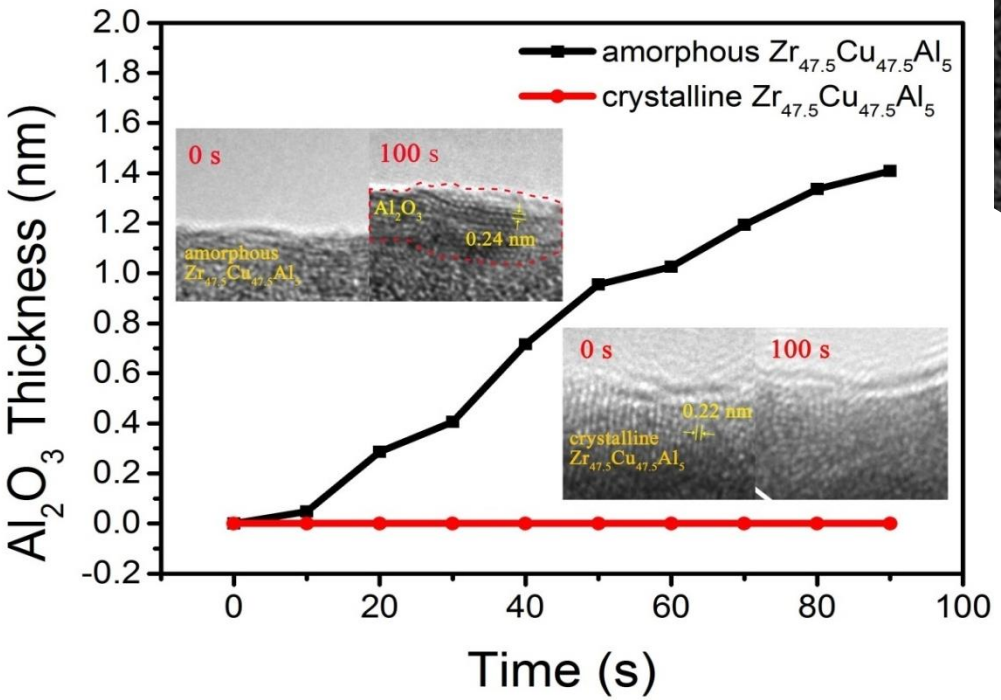
# Surface Diffusion

- Driven by gradients in chemical potential μ
  - Origin: Concentration, curvature, electric filed, temperature, pressure
  - Many applications: sintering, nanostructure stability, catalysis, surface crystallization, pharmaceuticals, candy
- Analysis Approach
  - Continuum
  - Atomistic
  - Simulation
- Continuum
  - All models follow the original approach from W. Mullins based on Capillarity. (J. Appl. Phys. 28(1957)333, 30(1959)77.)
  - For Crystals—Most often used to analyze the evolution of a thermal Groove at the intersection of a grain boundary with the free surface; also for the motion of pores and shape changes. Almost all reported results are for single component materials

# Free surface of $Zr_{47.5}Cu_{47.5}Al_5$




Aluminiferous metallic glass systems

**Fast surface dynamics effect of MGs**

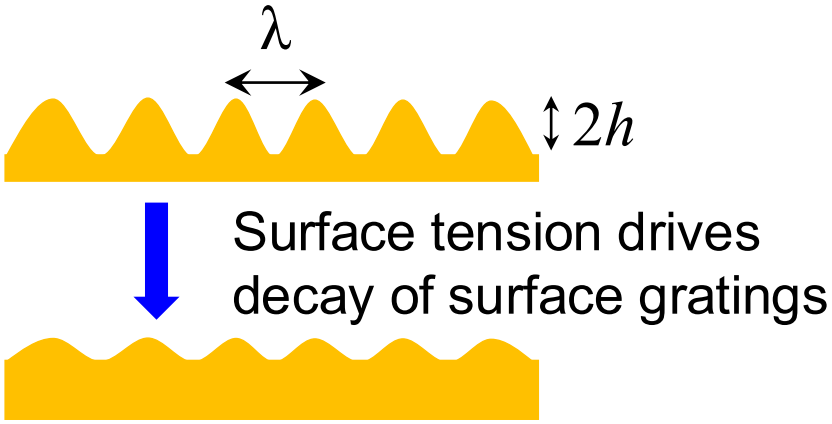
**At room temperature**

**Scripta Mater 136, 68 (2017)**

# Mullins Model Analysis

- Assumptions
- Transport mechanisms (surface, volume, vapor) act independently
- No loss of material
- $\gamma_s$ isotropic
- Small curvature
- Surface atomic structure is ignored

# Surface grating decay



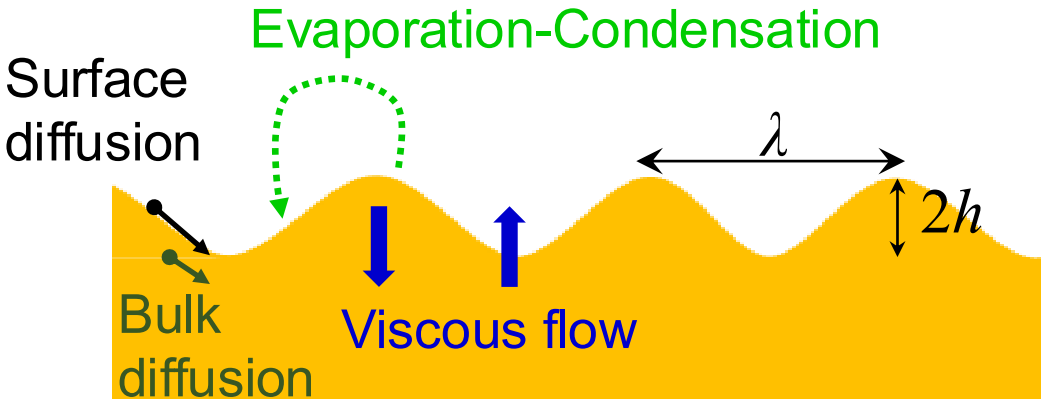

Decay kinetics is exponential:

$h/h_0 = \exp(-Kt)$

$h$: Grating amplitude

$\lambda$: Grating wavelength

$$K = F(2\pi/\lambda) + A(2\pi/\lambda)^2 + (A' + C)(2\pi/\lambda)^3 + B(2\pi/\lambda)^4$$




$$F = \frac{\gamma}{2\eta}$$

Viscous flow

$$C = \frac{D_v \gamma \Omega}{kT}$$

Bulk diffusion

$$A = \frac{p_0 \gamma \Omega^2}{(2\pi m)^{1/2}(kT)^{3/2}}$$

$$A' = \frac{\rho_0 D_G \gamma \Omega^2}{kT}$$

Evaporation-Condensation

$$B = \frac{D_s \gamma \Omega^2 \upsilon}{kT}$$

Surface diffusion

Mullins, W.W. *J. App. Phys.*, 1959, 30, 77–83

# Mullins model: surface grating decay

**Surface grating decay**

$$z(x,0) = h_0 \sin(qx)$$

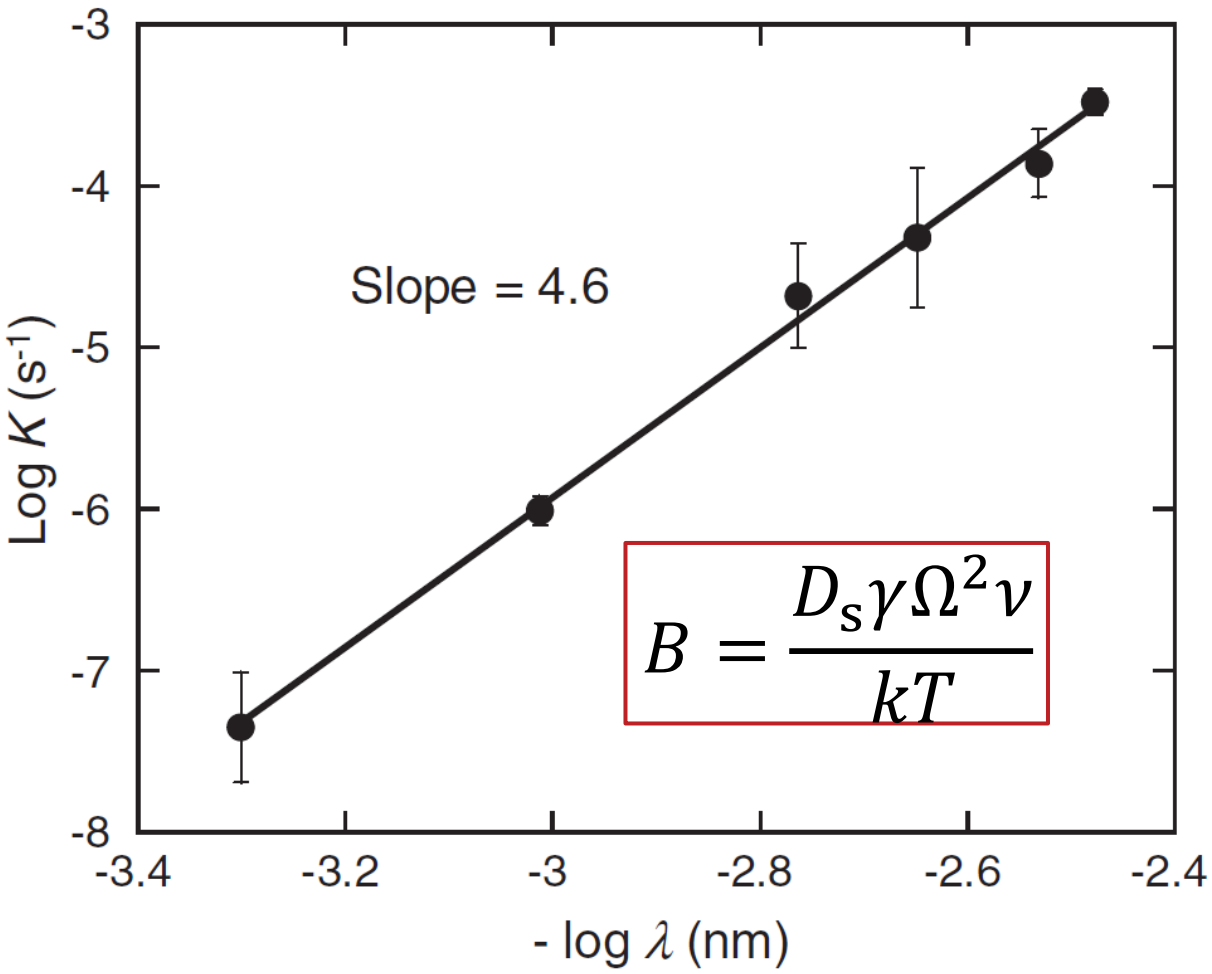
$$z(x,t) = h(t) \sin(qx)$$

$$h(t) = h_0 \exp(-Kt)$$

$$K = Fq + Aq^2 + Dq^3 + Bq^4$$

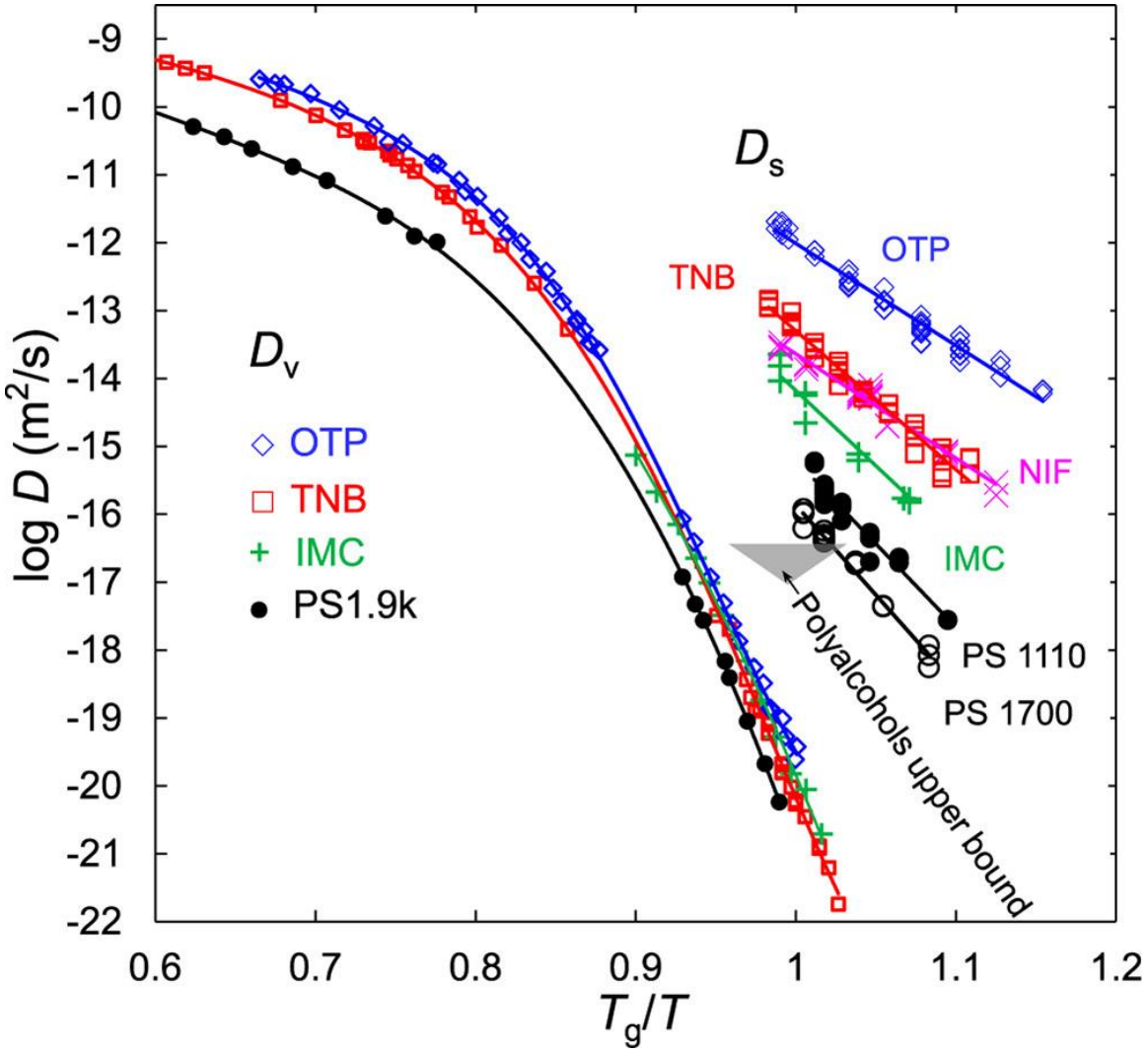
Other mechanisms

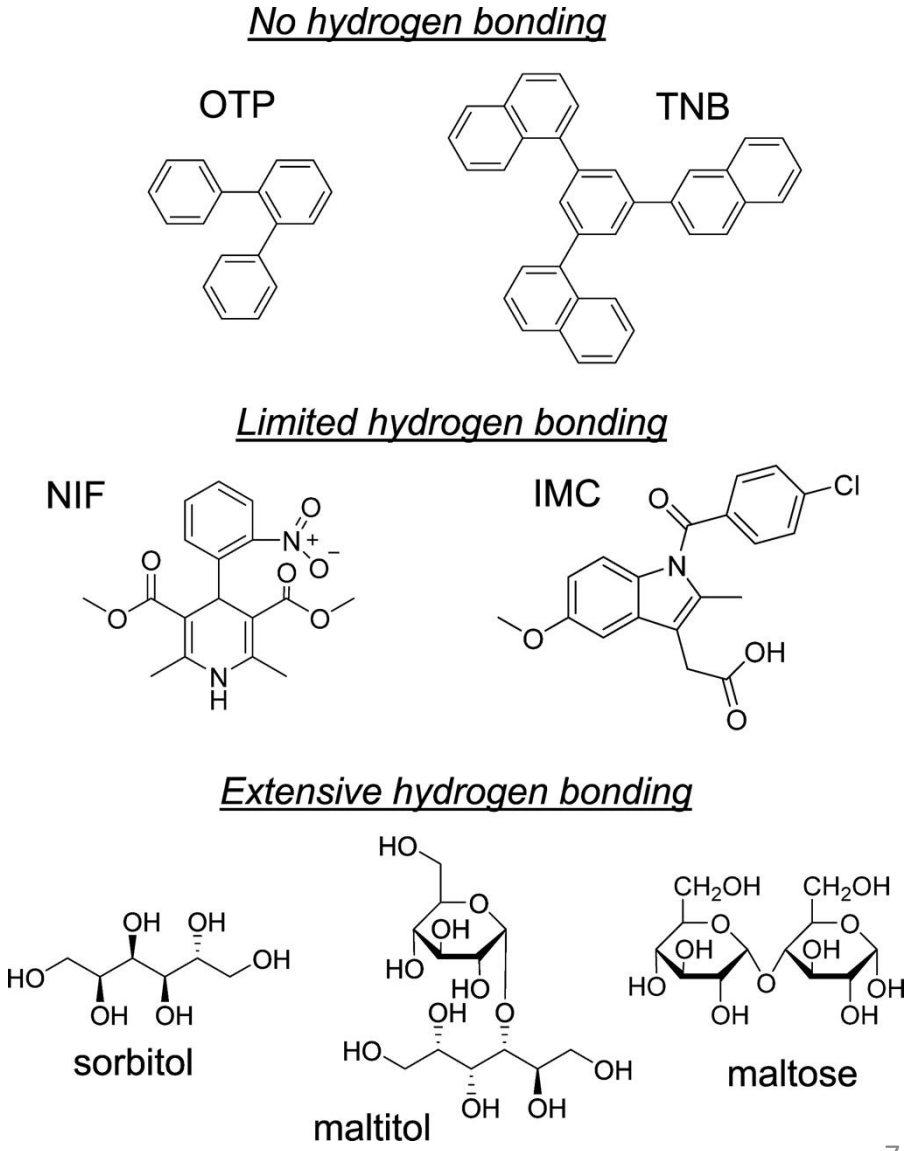
Surface diffusion




*J. Appl. Phys.* 30, 77, 1959
*Phys. Rev. Lett.* 106, 256103, 2011

# Enhanced surface diffusion in glasses



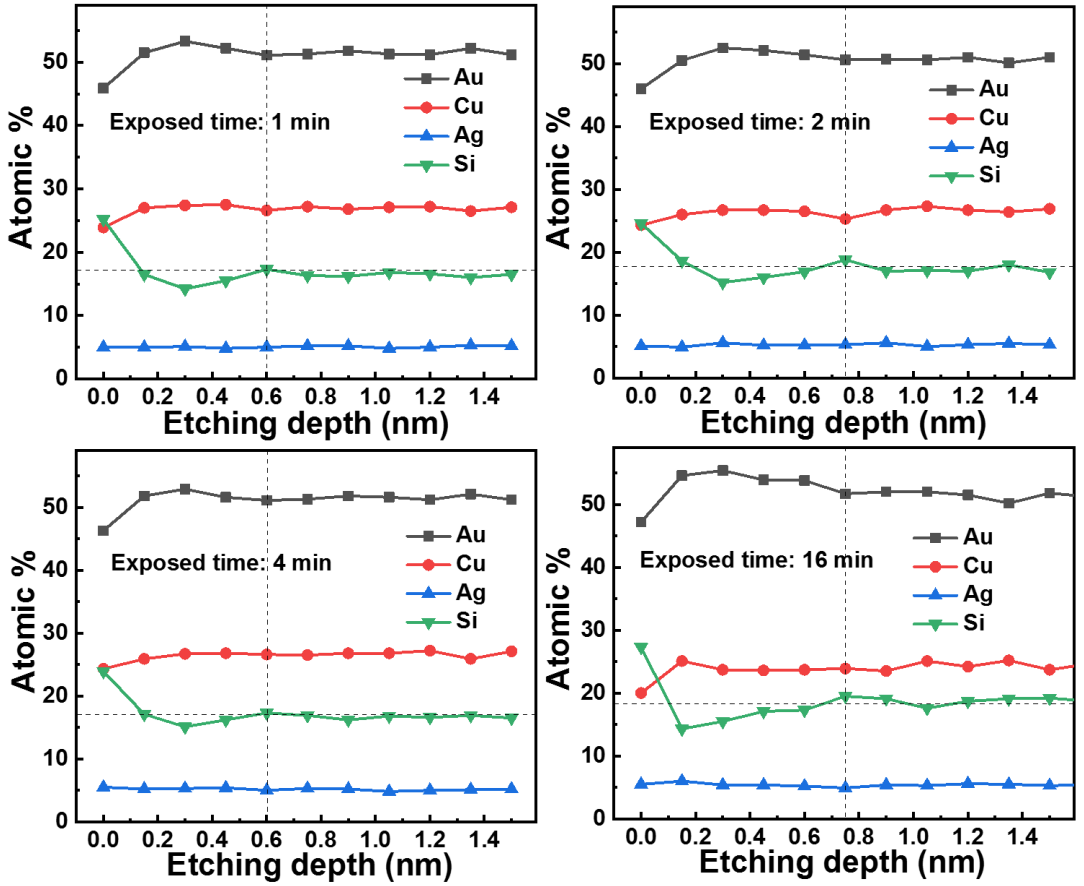




*J. Phys. Chem. B* 120, 8007, 2016

# Experimental Challenges for Metallic Alloys

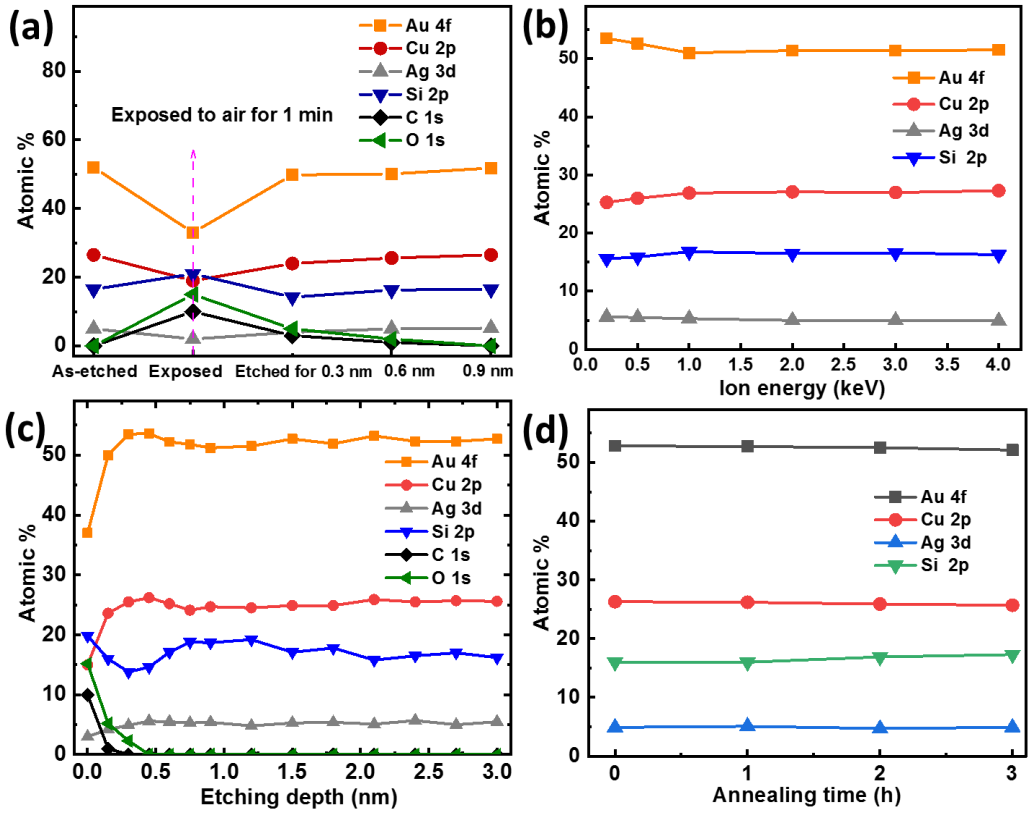
- Establishing a clean surface
- Avoid oxidation
- Consider the impact of surface segregation of components
- Annealing temperature must be low enough to avoid rapid surface crystallization, but high enough to promote surface diffusion
- Surface must be smooth (i.e. RMS ≈0.1 nm)
- Establishing a suitable surface profile
  - Periodic grating
    - Photolithography
    - Embossing – impressing a pattern near glass transition
    - AFM scratching- must avoid shear bands for metallic glass
- Other methods: FIM, nanoparticle sintering, STM
- Difficult but possible for single phase materials.

# Surface Exposure




XPS depth profiling quantitative composition analysis of the surface exposed to air for 1 min, 2 min, 4 min and 16 min, respectively.

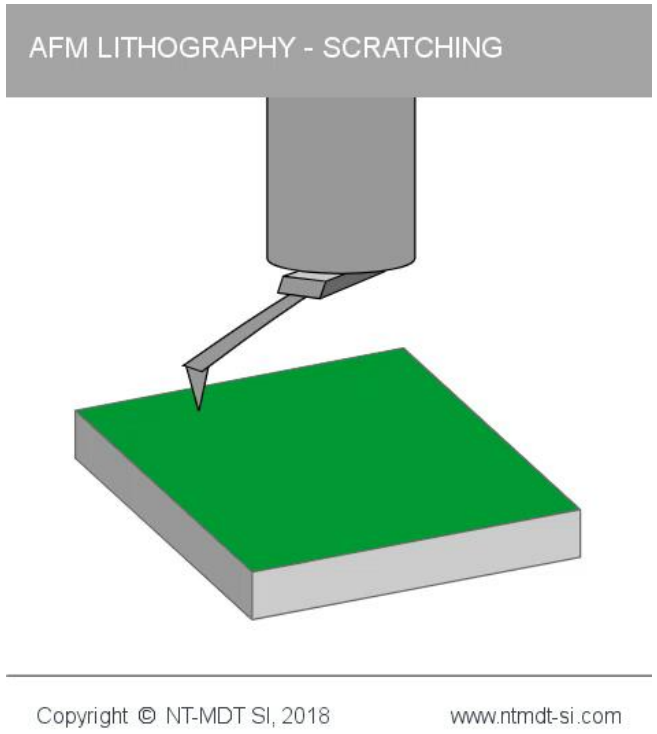
# Surface Treatment

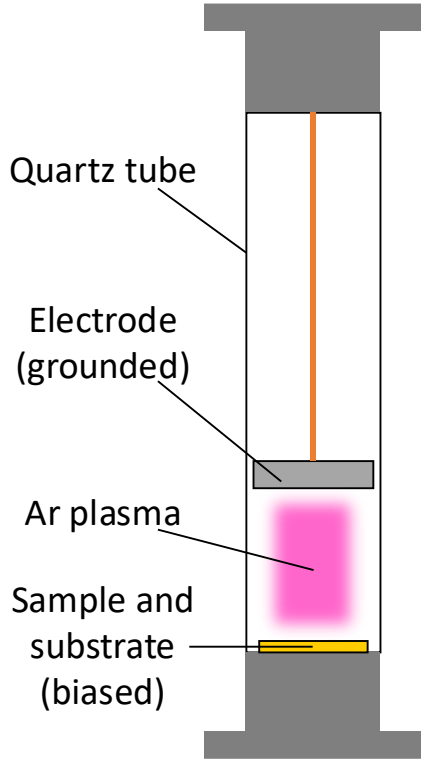


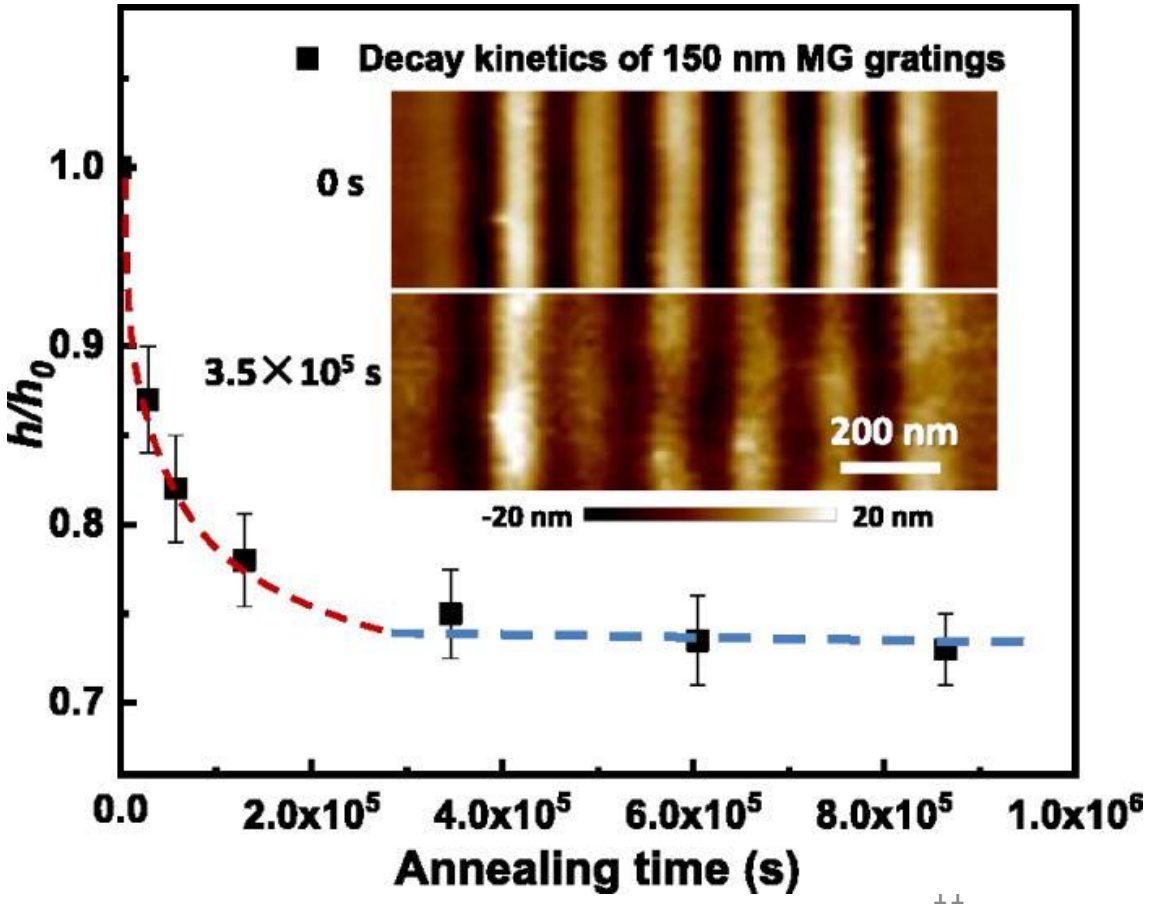

Surface composition analysis. (a) XPS depth profiling quantitative analysis of the Ar ion etched sample before and after 1 min exposure to air. (b) The influence of Ar ion beam energy on composition. (c) Compositional variation with the etching time history at the Ar plasma energy of 2 keV. (d) XPS in situ analysis of the surface composition variation with the annealing time history under high vacuum at room temperature.

# AFM lithography and *in situ* cleaning

- In situ argon plasma cleaning within a high-vacuum furnace
- Exponential grating decay followed by Si segregation



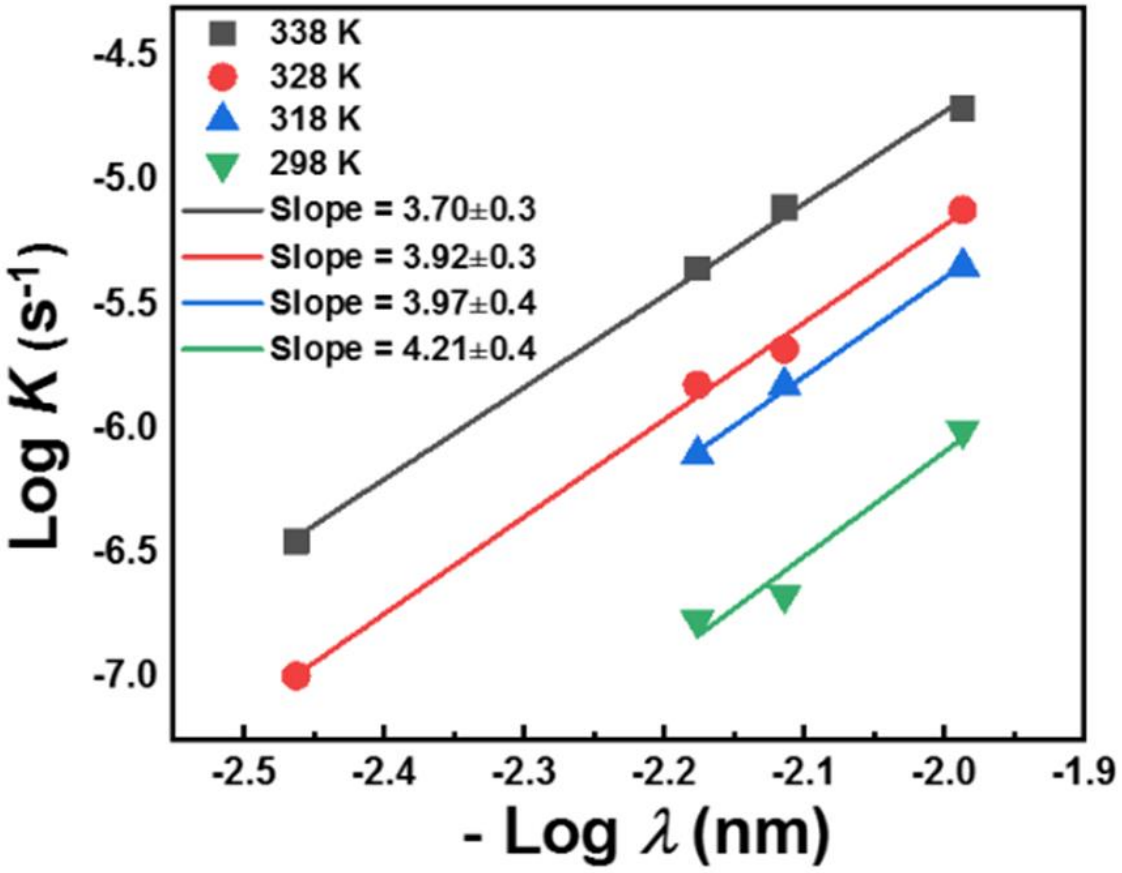



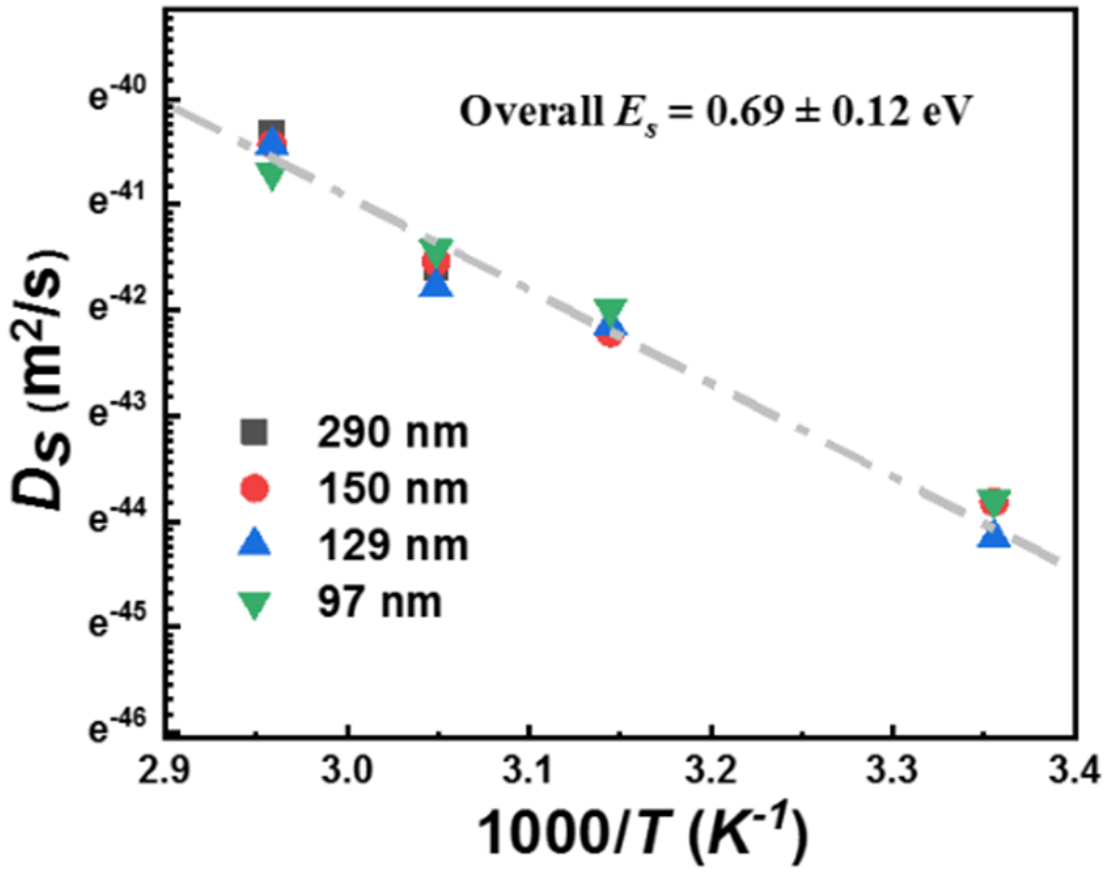




*Appl. Phys. Lett.* 116, 231601, 2020

# Activation energy for surface diffusion

- Surface diffusion governs grating decay at 0.83~0.94$T_g$
- Arrhenius temperature dependence of $D_s$ with $E_s$ = 0.69 ± 0.12 eV

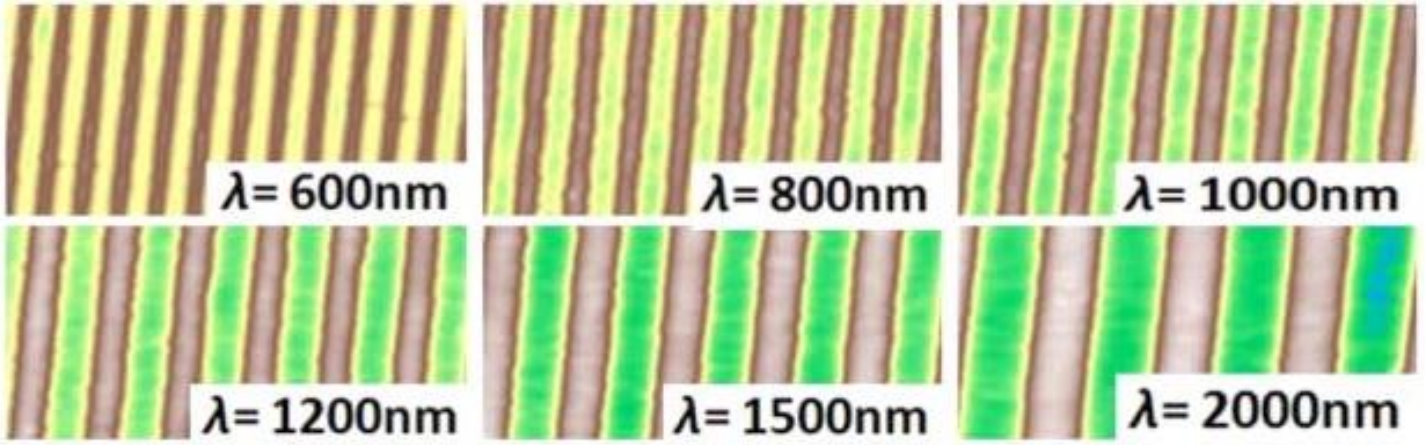


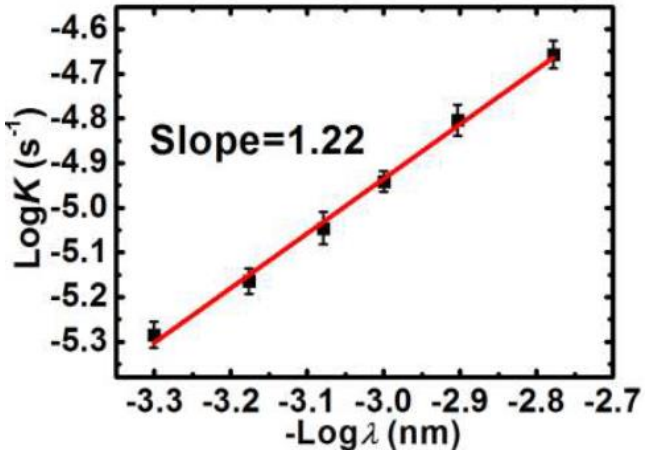




*Appl. Phys. Lett.* 116, 231601, 2020

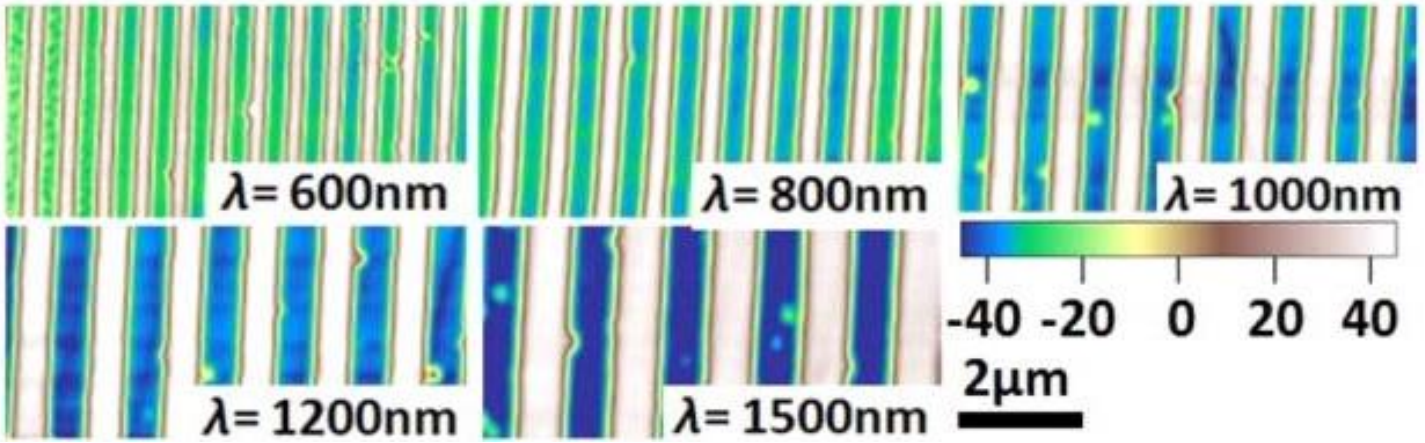
# Surface mobility of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MG

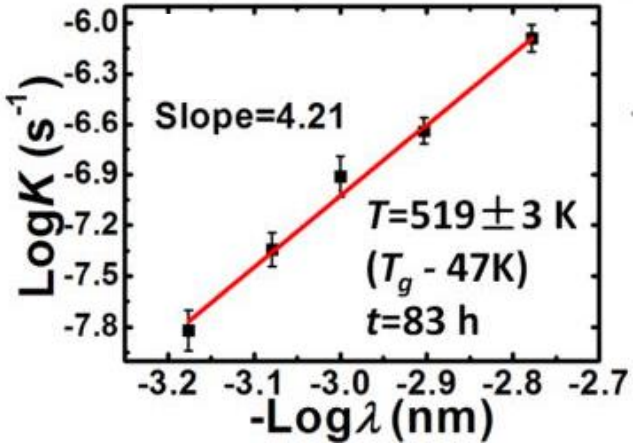
$T_g$ – 23 K for 16 h, viscous flow, $\eta$ = 5.83 × $10^{11}$ Pa s




$T_g$ – 47 K for 83 h, surface diffusion, $D_s$ = 1.23 × $10^{-16}$ $m^2$ $s^{-1}$

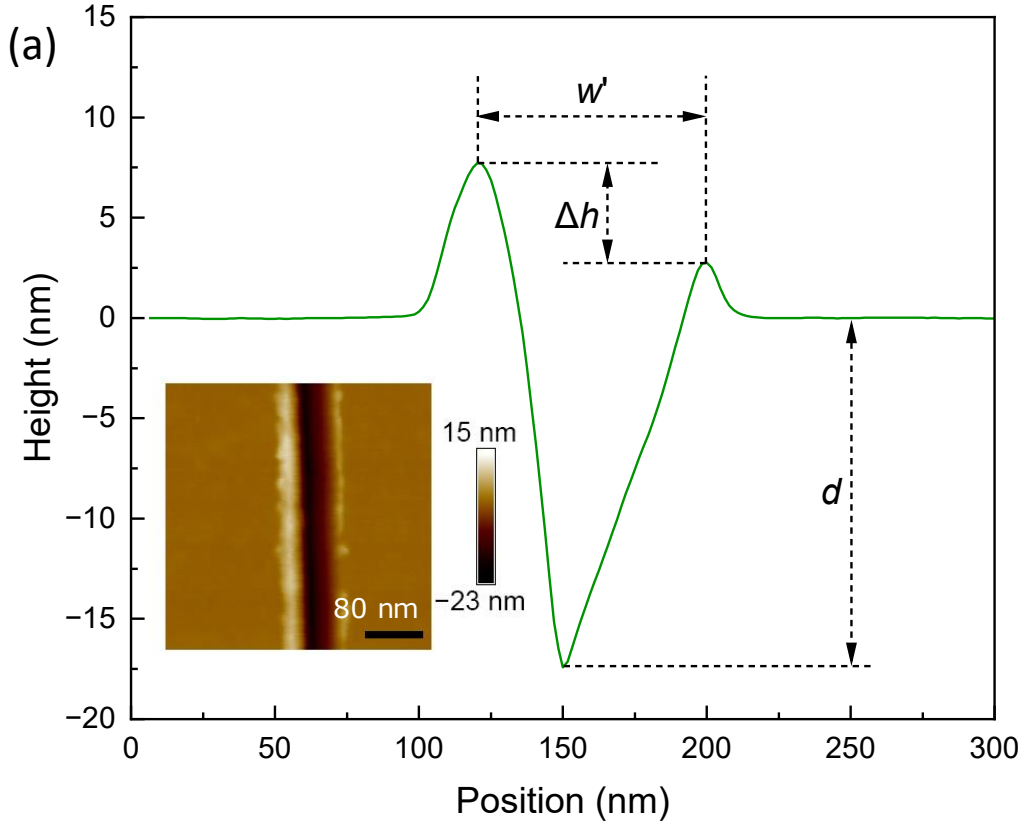


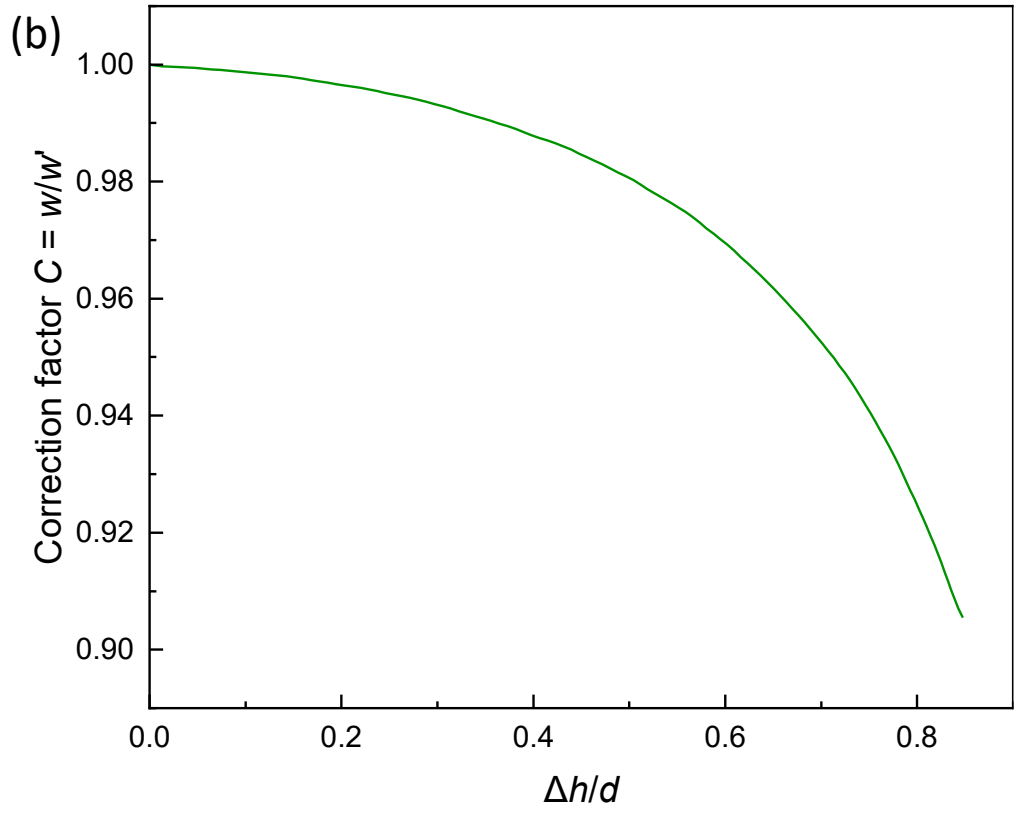




*Appl. Phys. Lett.* 107, 141606, 2015

# Mullins model: surface scratch decay

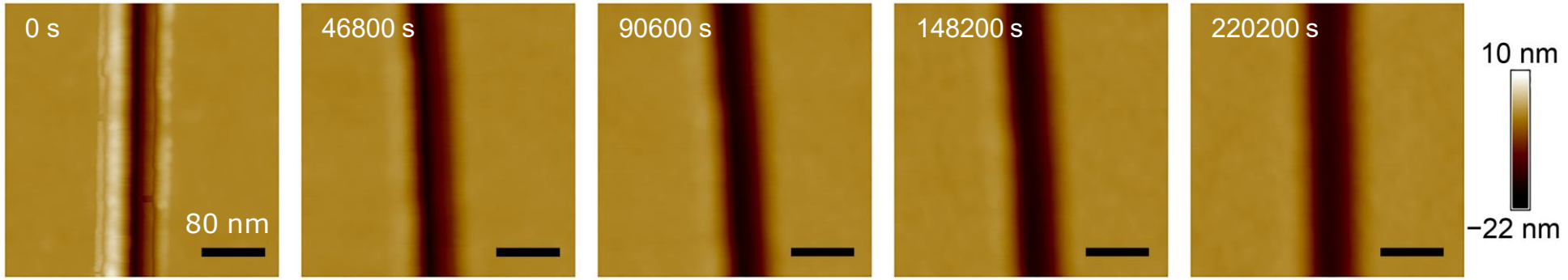
$$w = Cw' = 6.907[B(t + t_0)]^{1/4} \qquad B = \frac{D_s \gamma \Omega^2 \nu}{kT}$$

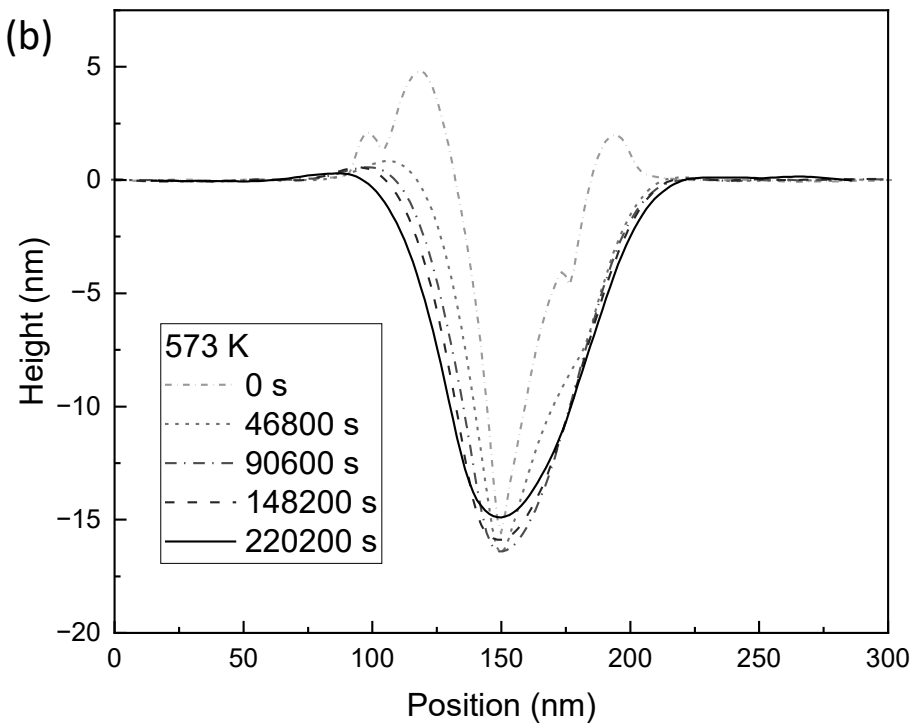


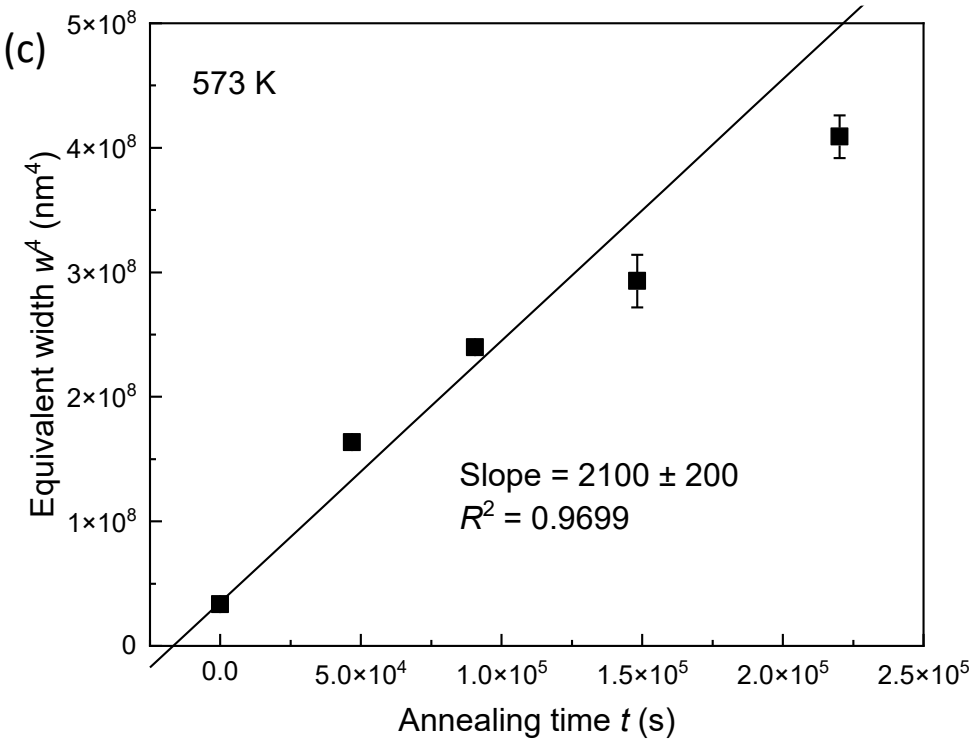




*Appl. Phys. Lett.* 124, 091601, 2024
*Acta Metall.* 10, 601, 1962; *Acta Metall.* 14, 397, 1966

# Surface scratch smoothing process



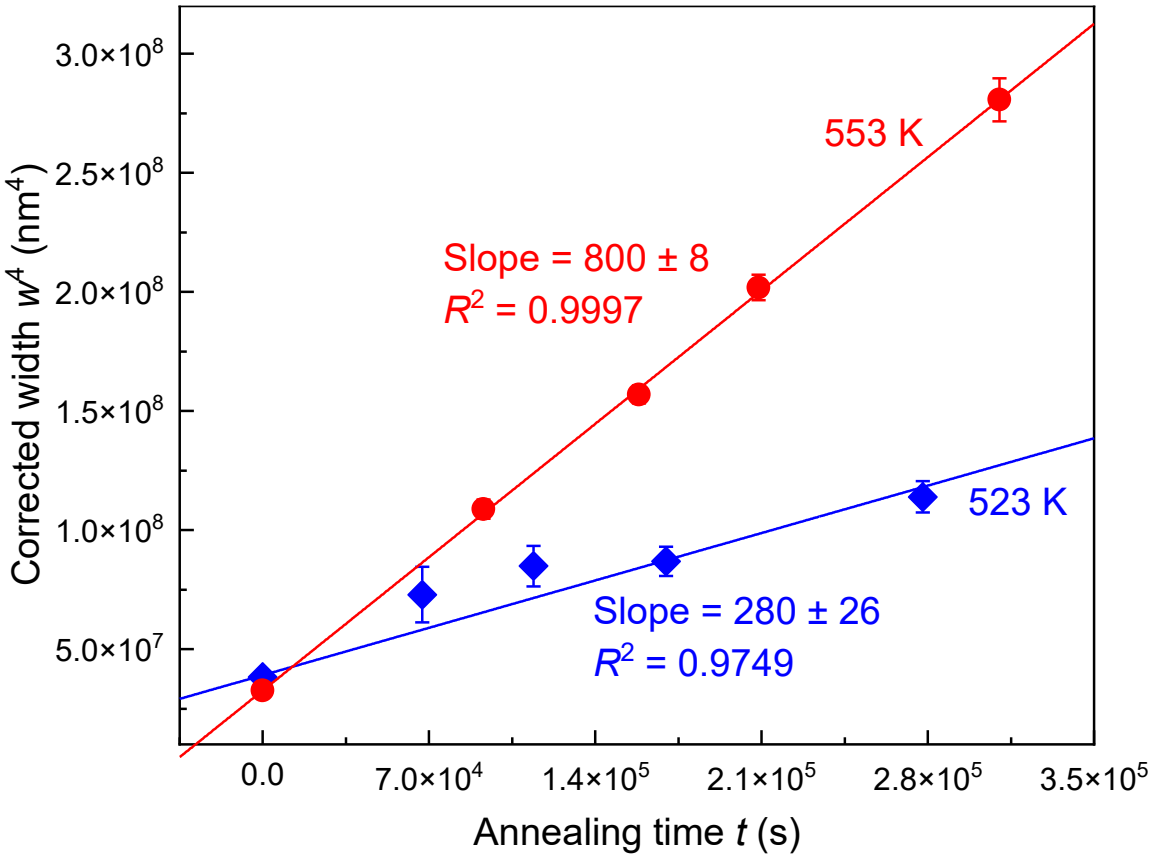



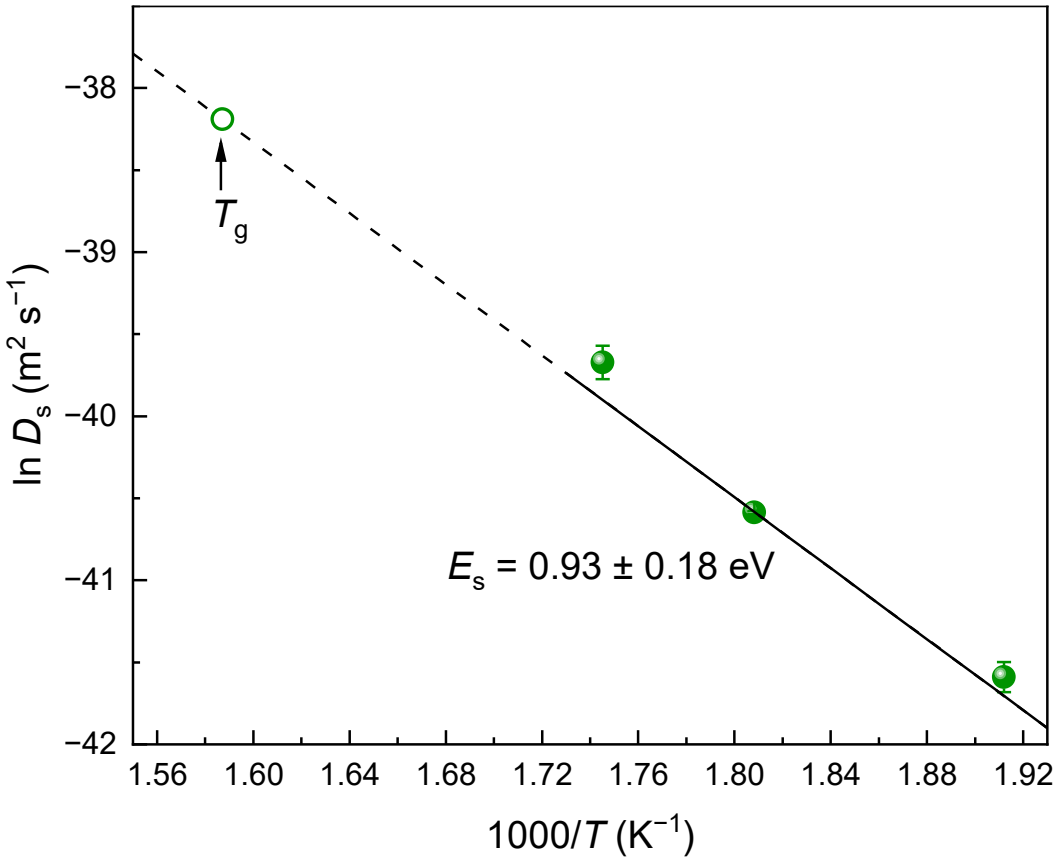




*Appl. Phys. Lett.* 124, 091601, 2024

# Activation energy for surface diffusion

- Surface diffusion governs scratch decay at 0.83~0.91$T_g$
- The $E_s$ = 0.93 ± 0.18 eV is about half that for bulk diffusion

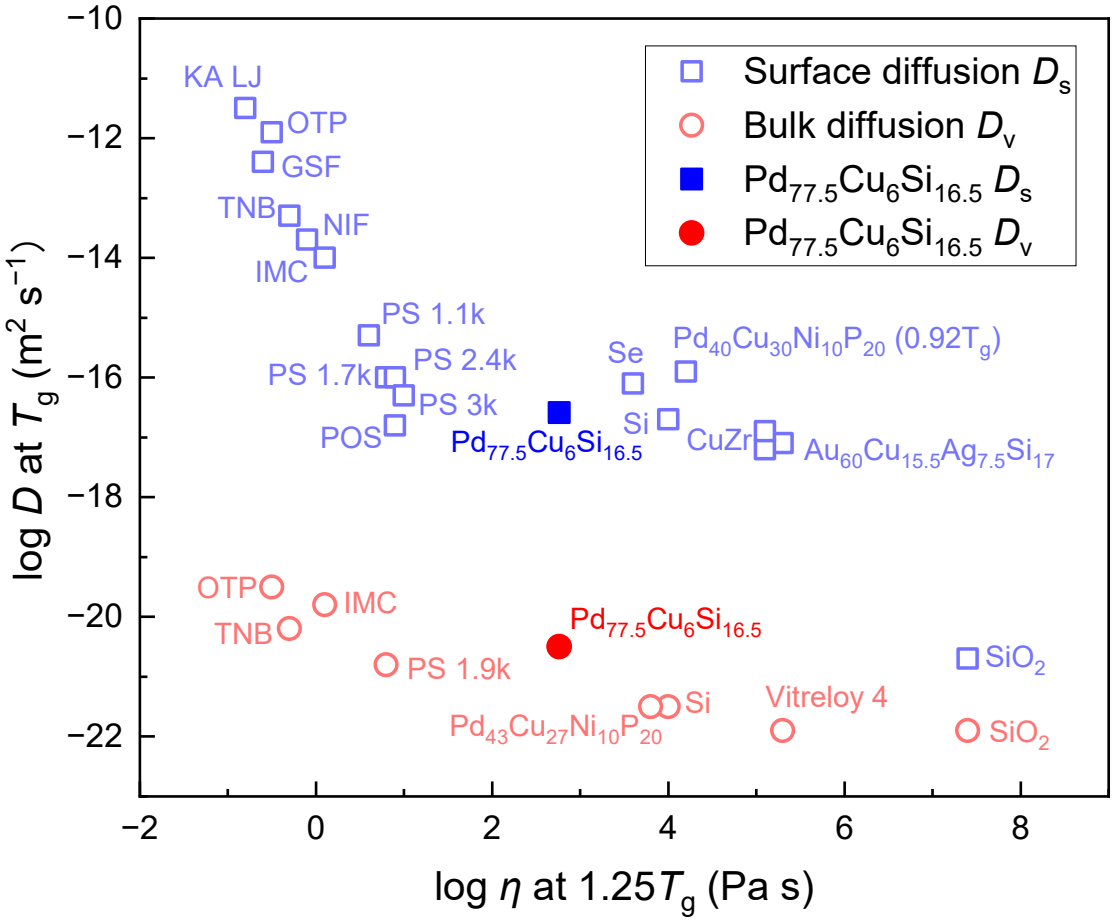


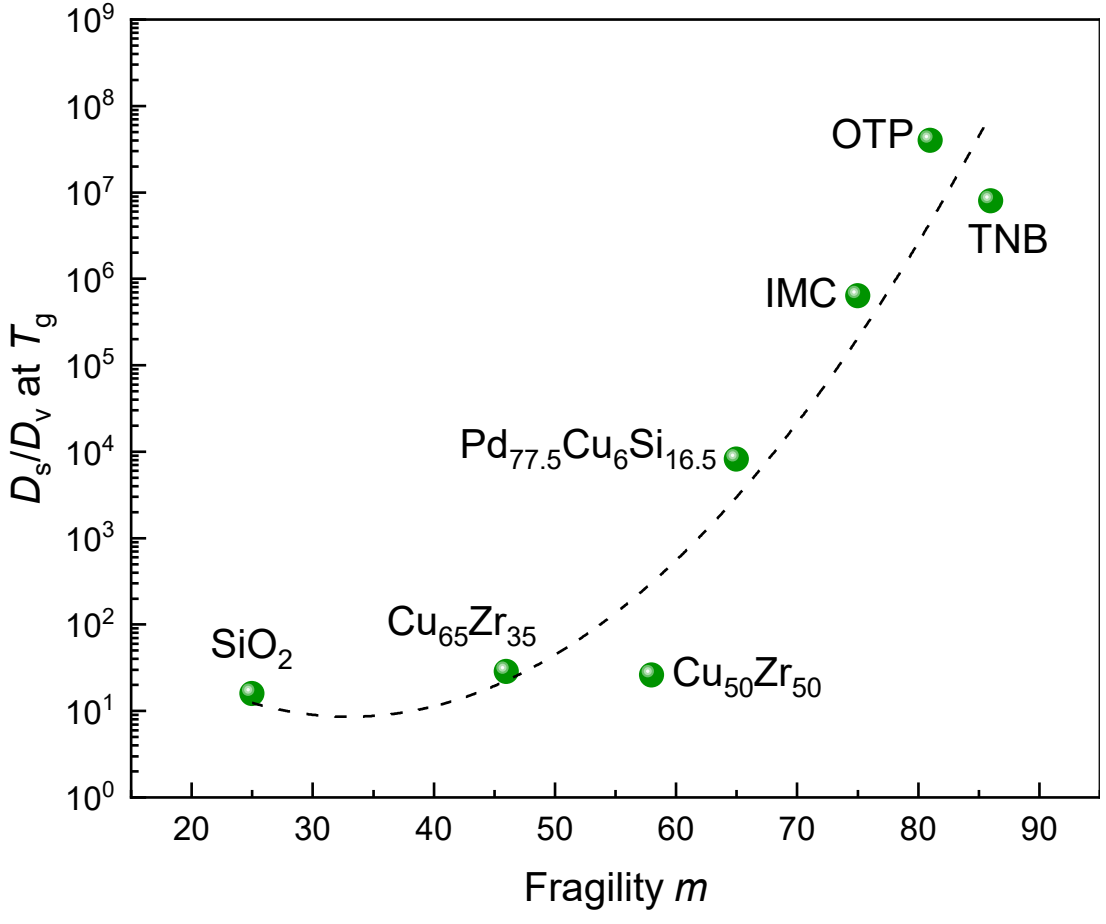




*Appl. Phys. Lett.* 124, 091601, 2024

# Fragility vs Enhanced surface diffusion

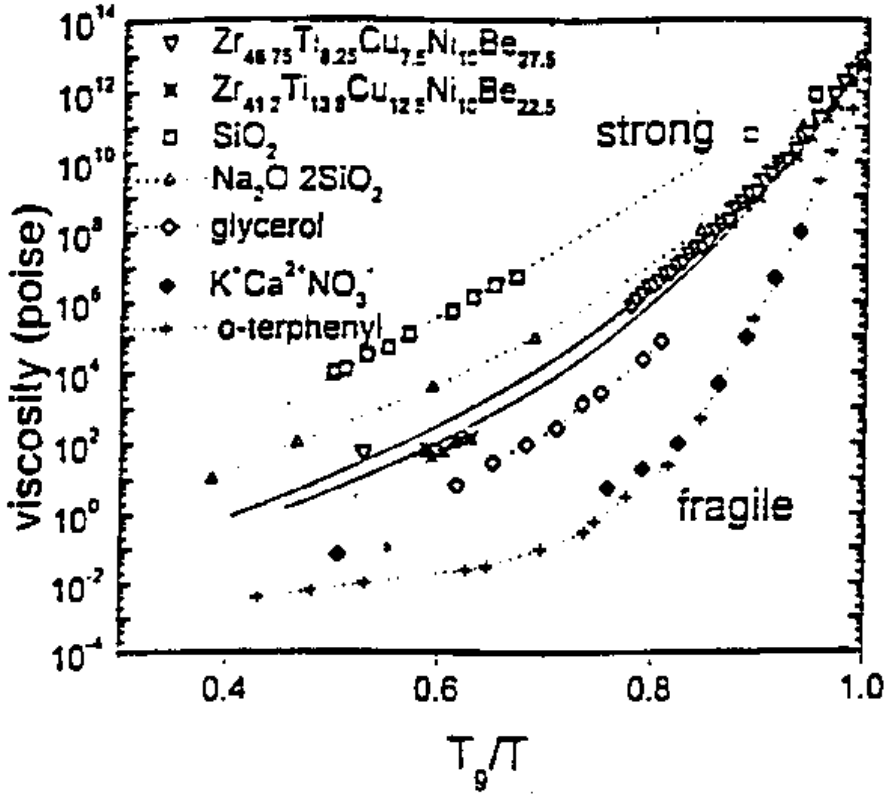
The two kinds of dynamic excitations are related to the interactions at the atomic or molecular level.

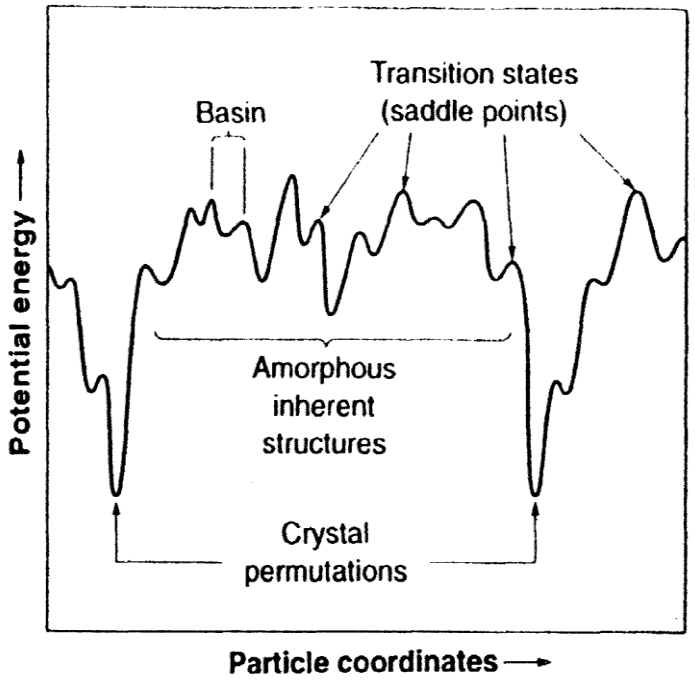


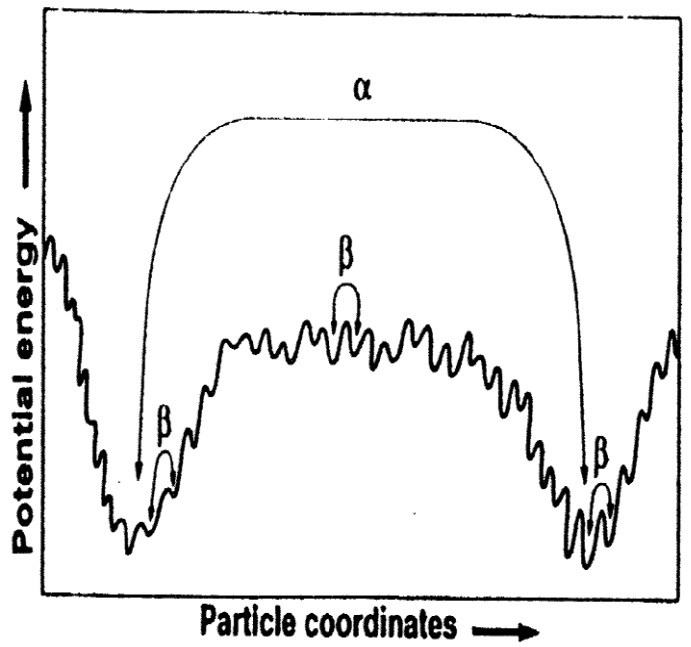




*Phys. Rev. Lett.* 128, 075501, 2022; *Appl. Phys. Lett.* 124, 091601, 2024

# Glass Dynamics



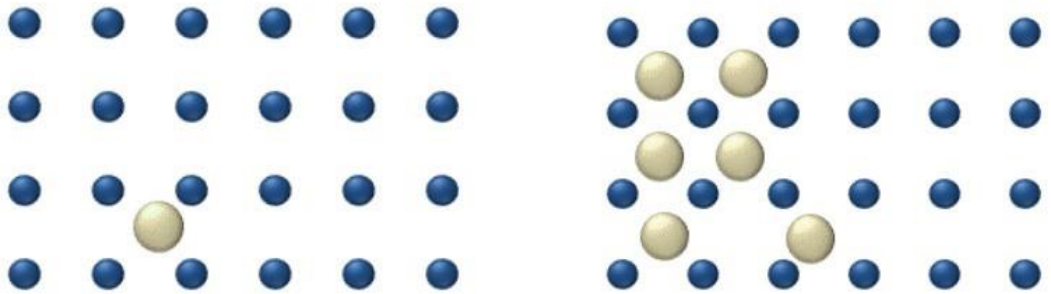



# Summary of $D_s$ measurements in MGs

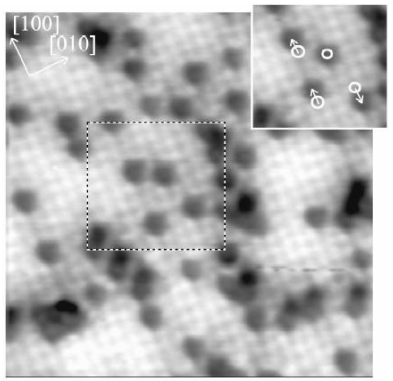
| **MG composition ($T_g$)** | **Methods** | ***T*** | **$D_s$ ($m^2\ s^{-1}$)** | **$E_s$ (eV)** |
|---|---|---|---|---|
| $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (566 K) | Surface grating decay e-beam lithography + dry etching | $0.92T_g$ | $1.23 \times 10^{-16}$ | N/A |
| $Au_{60}Cu_{15.5}Ag_{7.5}Si_{17}$ (358 K) | Surface grating decay AFM lithography + in-situ cleaning | $0.83 \sim 0.94T_g$ | $(9.0 \pm 2.1) \times 10^{-20}$ ~$(2.6 \pm 0.5) \times 10^{-18}$ | $0.69 \pm 0.12$ |
| $Pd_{77.5}Cu_6Si_{16.5}$ (630 K) | Surface scratch decay AFM lithography + in-situ cleaning | $0.83 \sim 0.91T_g$ | $(8.7 \pm 0.8) \times 10^{-19}$ ~$(5.9 \pm 0.6) \times 10^{-18}$ | $0.93 \pm 0.18$ |

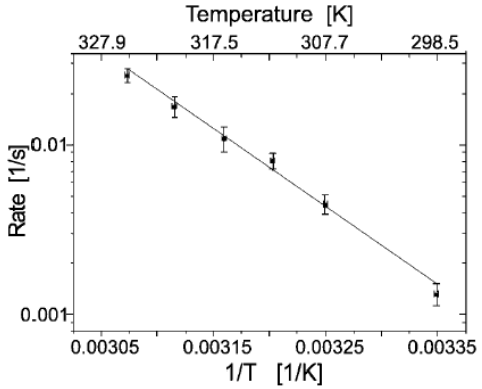
# Atomistic Mechanisms

**1) Hopping mechanism:**



• Example: N adatoms on Fe(100) (Pedersen et al., PRL 2000)

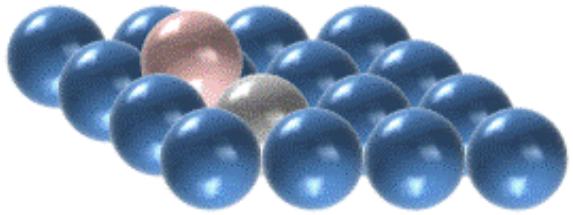


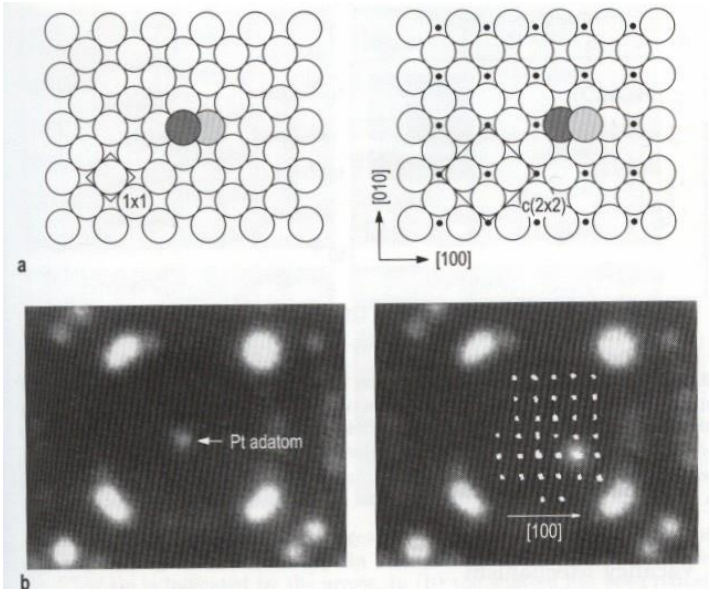

☒ Arrhenius law with $\nu \sim 10^{12}$ s$^{-1}$, $E_{diff}$ = 0.92 eV

# Atomistic Mechanisms

**2) Atomic exchange mechanism**:



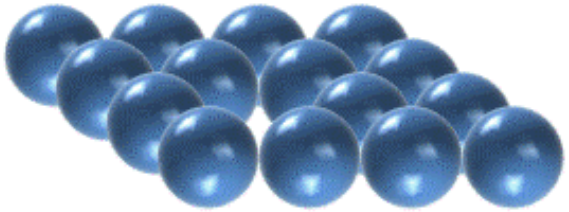
•Example: Pt adatom on Pt(100)
(Kellogg, SSR 1994)



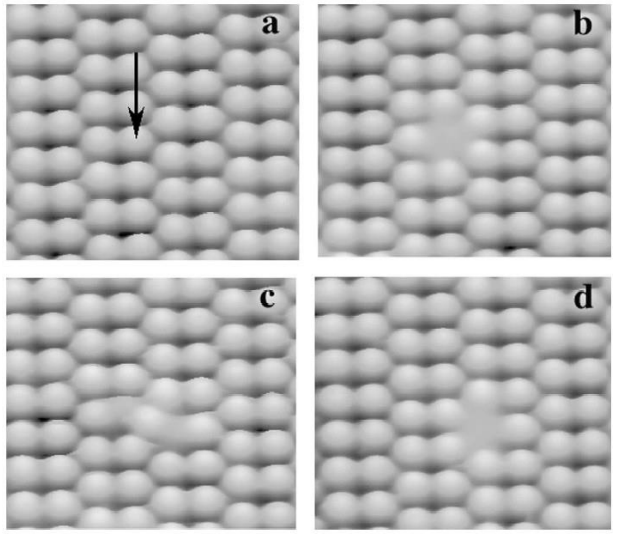

• Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

# Atomistic Mechanisms

**4) Vacancy mechanism**:



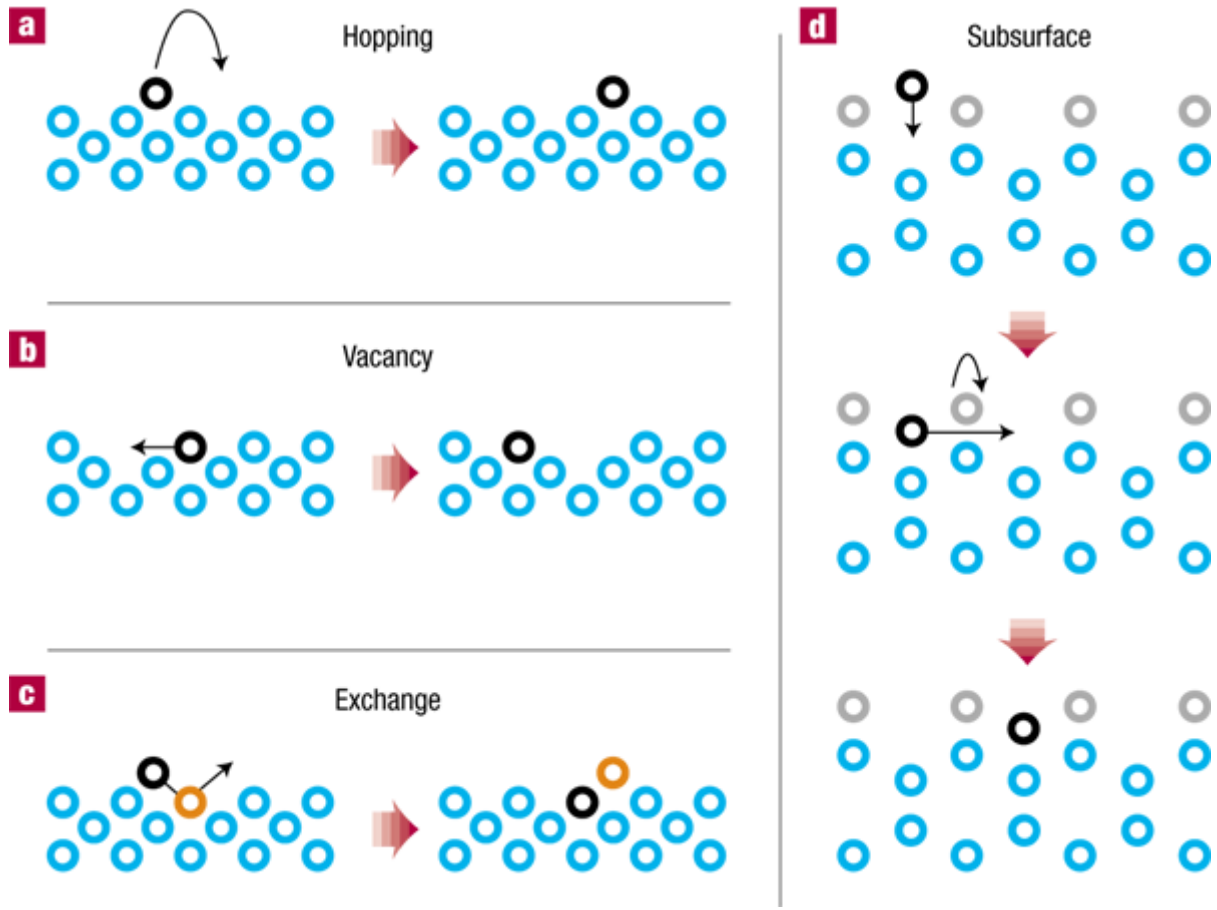
• Example: Ge(111)c(2x8) (Mayne et al., SS 2001)




-Vacancy created with the STM tip

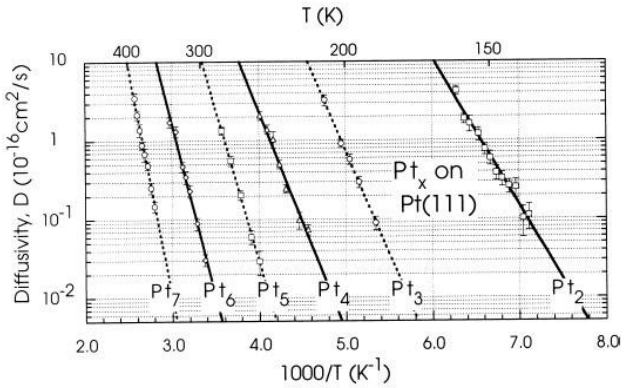
- T-activated hopping of neighboring atoms

• Heterodiffusion by vacancy-exchange also reported

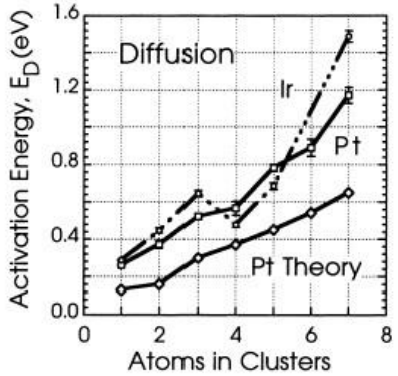

a
Hopping
b
Vacancy
c
Exchange
d
Subsurface

# Cluster Diffusion

- The larger the cluster, the lower its mobility:

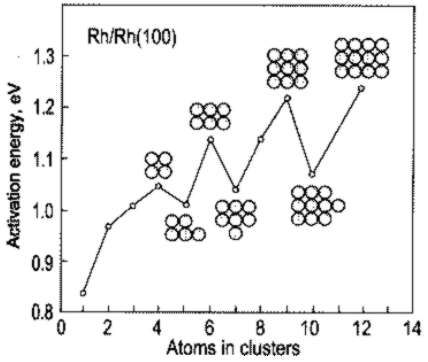



- <u>Activation energy increases</u> with cluster size:




(Kyuno & Ehrlich, SS 1999)

- Compact shapes are less mobile...



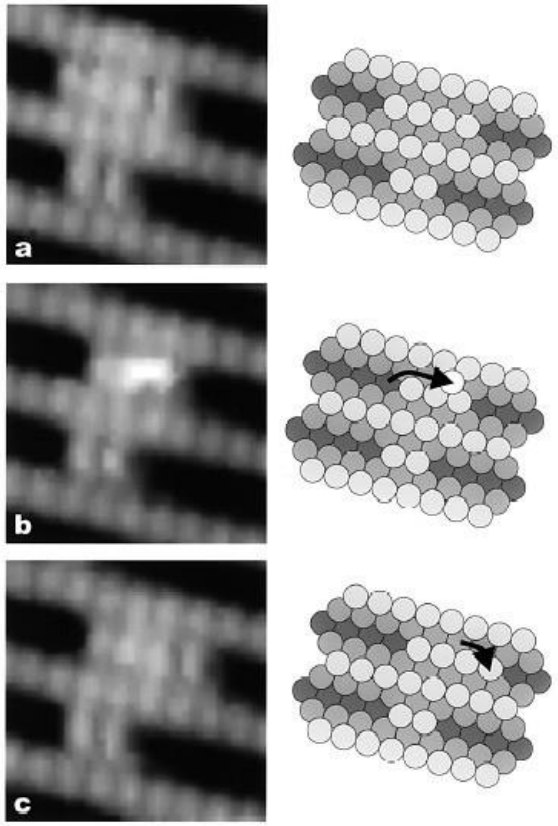

(Kellogg, PSS 1996)

# Cluster Diffusion

**Individual mechanisms:**

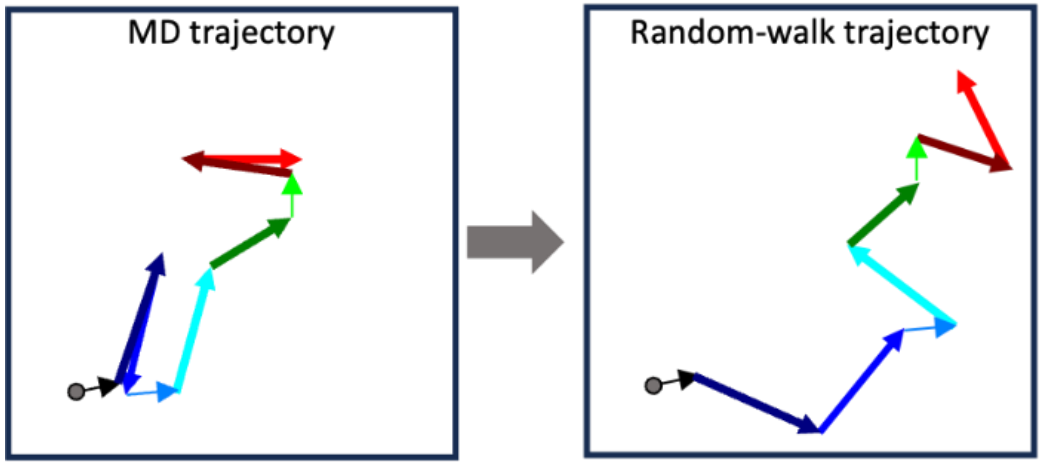
(4) “Leapfrog” mechanism:

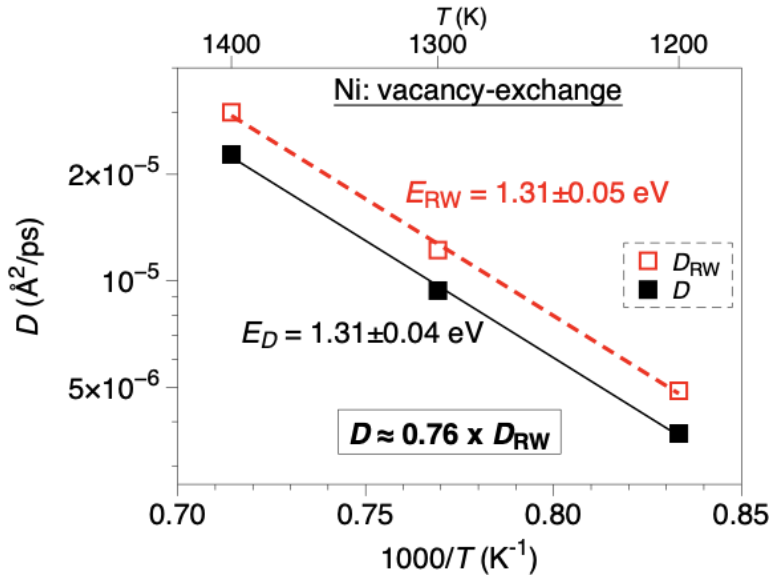
•Example: Pt(110)2x1
(Linderoth et al., PRL 1999)



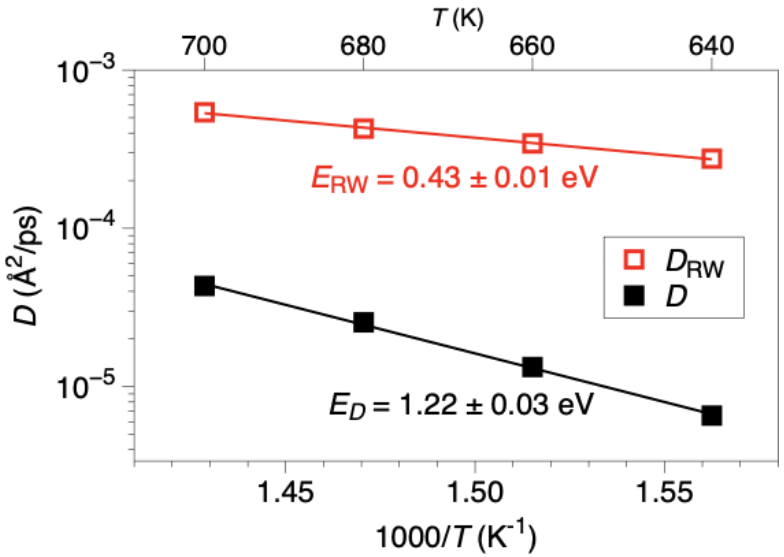
# Random-walk Diffusion ($D_{RW}$)

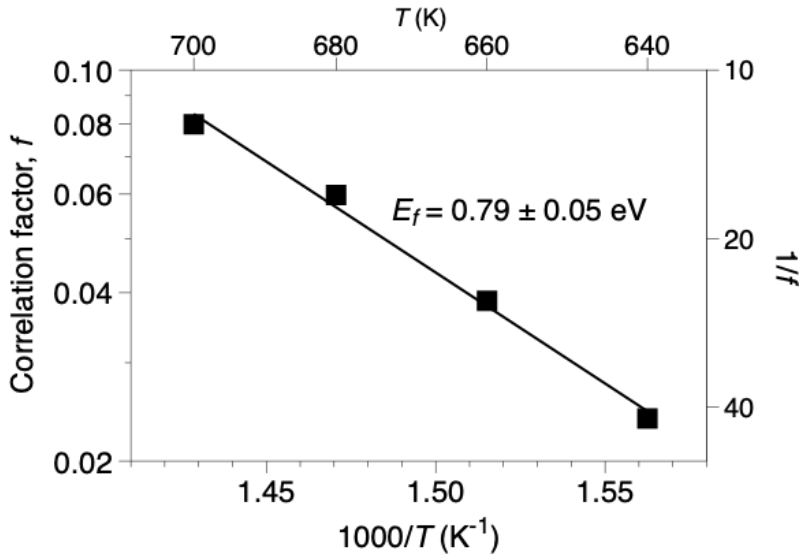
- For each atom in our MD simulation, a hypothetical random-walk trajectory is constructed using its short-time displacements.
- This gives a random-walk diffusion, $D_{RW}$ which represents diffusion in the absence of correlations.
- We then define a correlation factor, $f = D/D_{RW}$, which quantifies how much correlations modify diffusion.



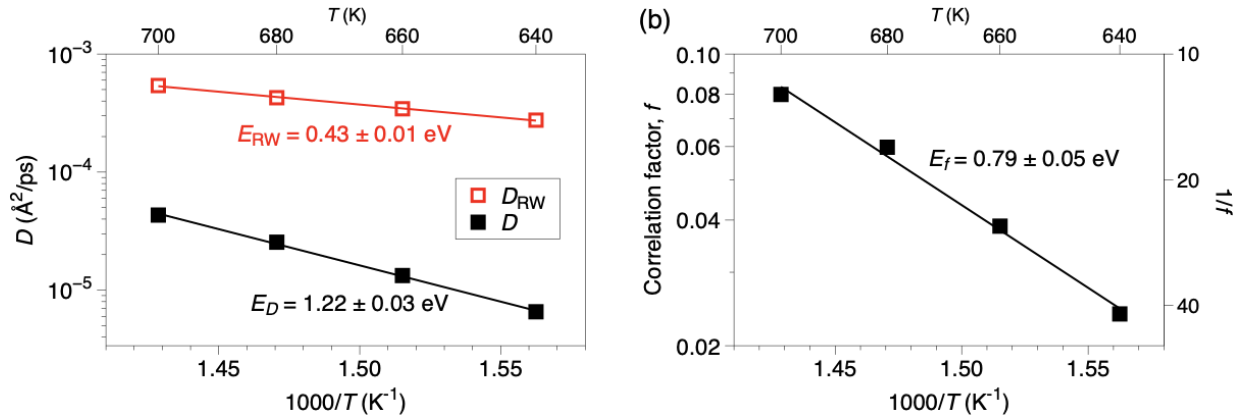
# Correlation factor in $Cu_{50}Zr_{50}$



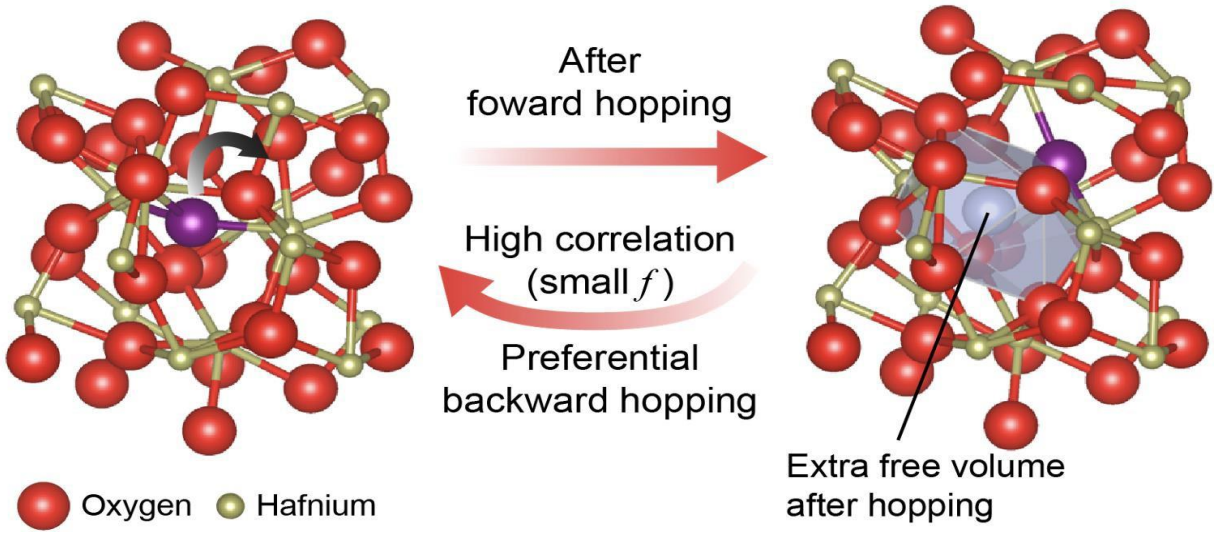




- Long-time dynamics slows down much faster than short-time dynamics (similar to α- and β-relaxation times).
- However, this additional slowdown is captured entirely by the correlation factor, *f* which decreases strongly with cooling, and there is a clear interpretation for *f.*
- *f* quantifies the extent of back-and-forth, or reversible, motion.

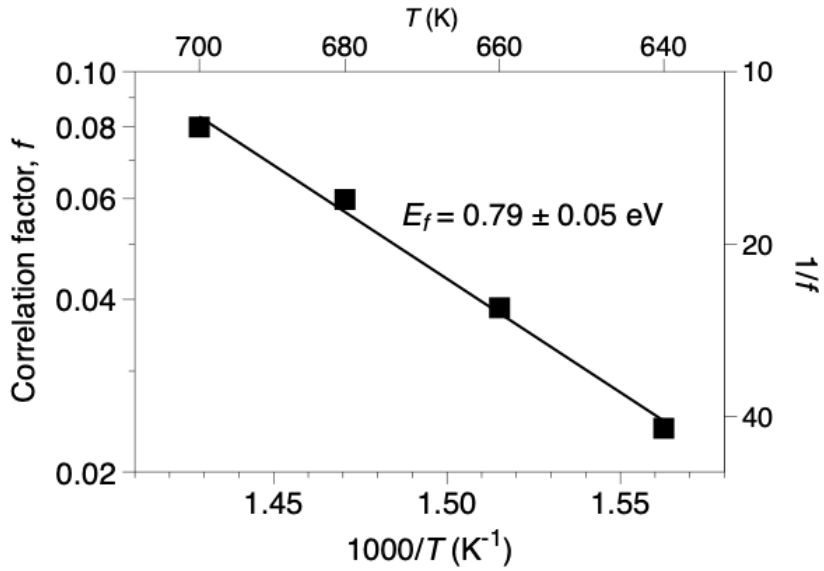
# Correlated Motion Underlies Slowdown in Glasses




- The slowdown of long-time dynamics is not primarily due to fewer rearrangements, but due to increasing reversibility of motion at lower temperatures.



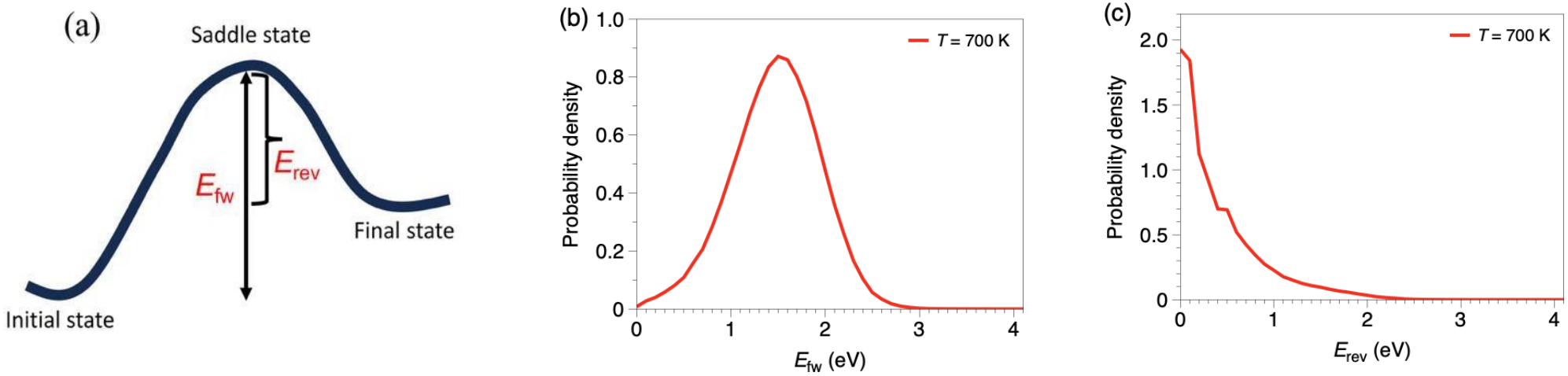
# Asymmetric Rearrangement Barriers Underlie Decreasing *f* with Cooling




- What leads to lowering of *f* with cooling?
- Potential energy landscape underlies this.

# Asymmetric Rearrangement Barriers Underlie Decreasing *f* with Cooling

- What leads to lowering of *f* with cooling?
- Potential energy landscape underlies this.




- Because reverse barriers are typically lower, a forward rearrangement is more likely to be undone than followed by a different forward move, leading to back-and-forth motion.

- This tendency increases with decreasing temperature, leading to a lower *f*.

# Summary

- Surface Diffusion is important for glass stability
- Measurement Methods and Analysis are well established for organic and metal one component systems
- For metallic glasses there are some challenges
  - Metallic glasses are multicomponent
  - Periodic grating may work, but grating synthesis can alter composition
  - Surface scratch approach appears to be promising
  - Surface crystallization, oxidation and segregation must be avoided
  - $D_s\gamma_s$ is measured, but for what component and what is the value for $\gamma_s$
  - Limited measured $D_s$ for alloys.
  - Correlation is an important factor in analysis.
  - Opportunities for analysis of alloy behavior.