Corrosion Science at the Nanoscale: Developing a Mechanistic Understanding of Materials Reliability

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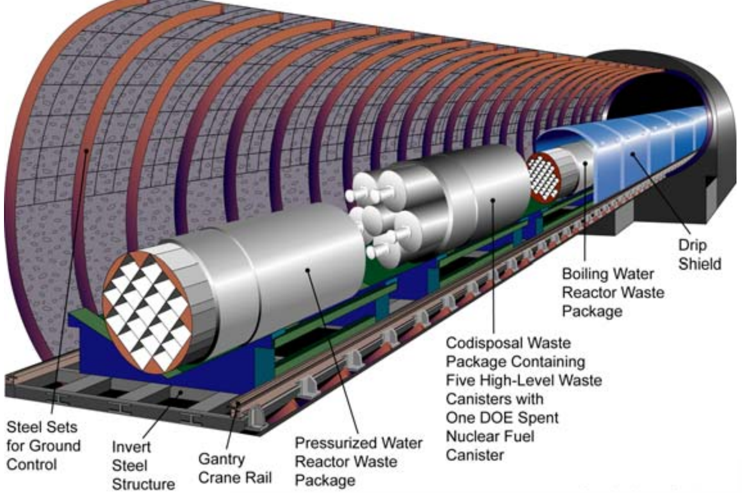
DOE Basic Energy Sciences Office of Materials & Engineering Sciences

National Nuclear Security Administration

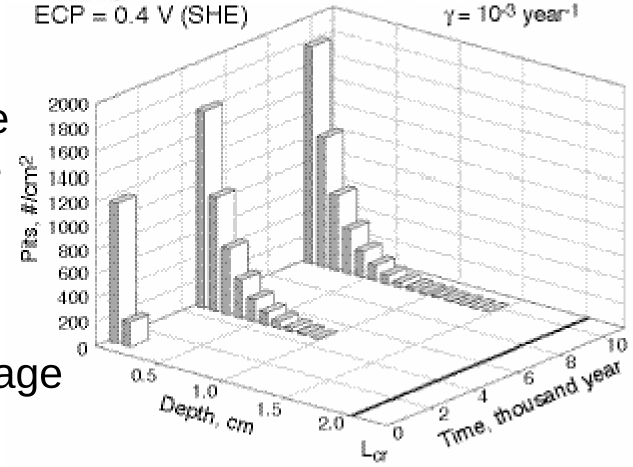
Sandia National Laboratories

Accurate prediction of the impact of corrosion is required in high consequence applications

Yucca Mountain engineered barriers require 10^6 yr lifetimes: Ni-Cr-Mo alloys

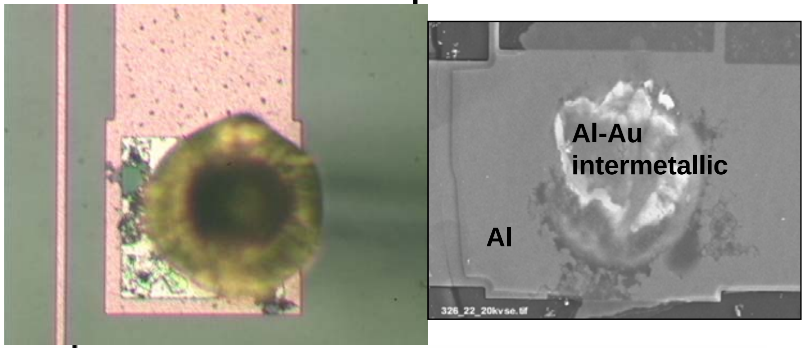


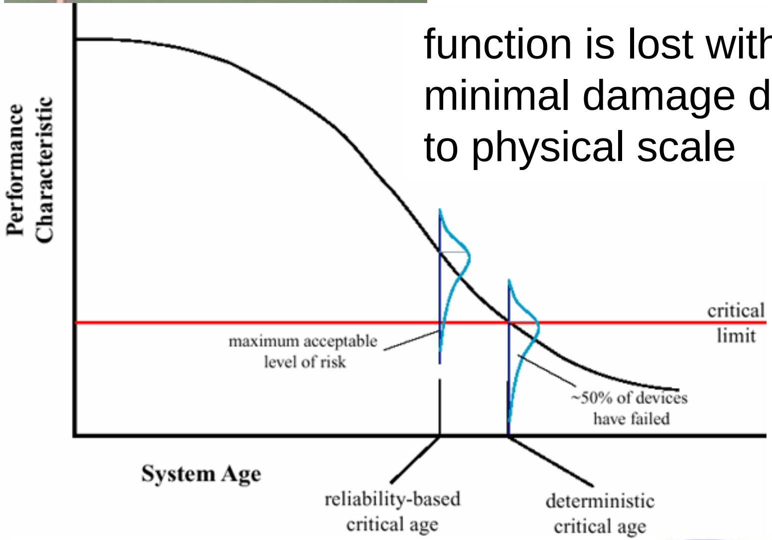
ultra-low rate processes are important due to time scale



localized damage prediction

Microelectronic devices in weapon systems require 10^1 yr lifetimes: Al interconnects are prevalent

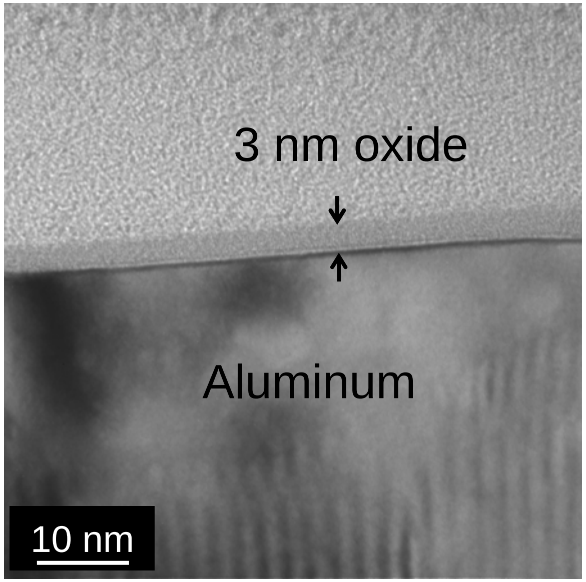




function is lost with minimal damage due to physical scale

accurate prediction requires relevant physical & chemical inputs

Corrosion results from a significant attenuation or loss of passivity



ΔG^{o}_{oxide}: -1852 kJ·mol^{-1}

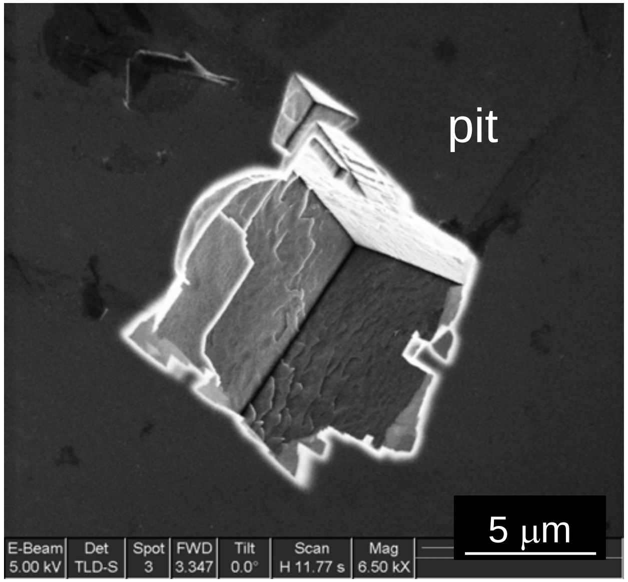
Rate $\propto \delta Al^{3+}/\delta t \propto k_o e^{-nFE/RT}$

the passive oxide regulates both electronic & mass transport at the interface

Corrosion can be uniform or localized

Chloride anion is a critical agent in localization resulting in pitting

Pit initiation location is considered random – site observation is very difficult



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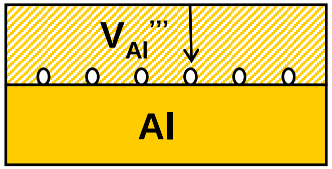
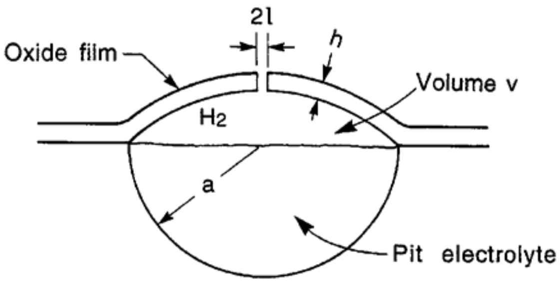
Current models of localized anodic dissolution processes do not adequately explain site specificity

Models invoke either intrinsic or evolving defects as specific sites for initiation

Pit initiation:



[1]vacancy condensation – PDM (D. Macdonald)

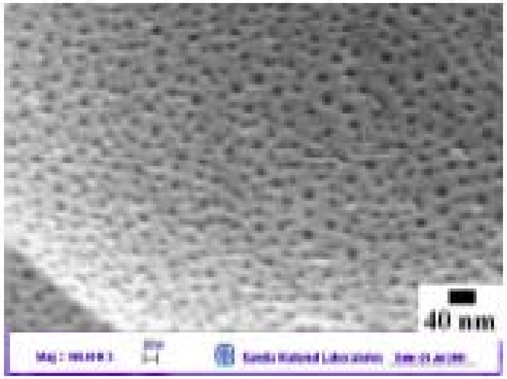


[2]nano-corrosion cells (McCafferty)

[3]thinned oxide structure
[4]flaws

Does nanostructure act as pitting site precursors?

The location of pore initiation is also viewed as defect driven:

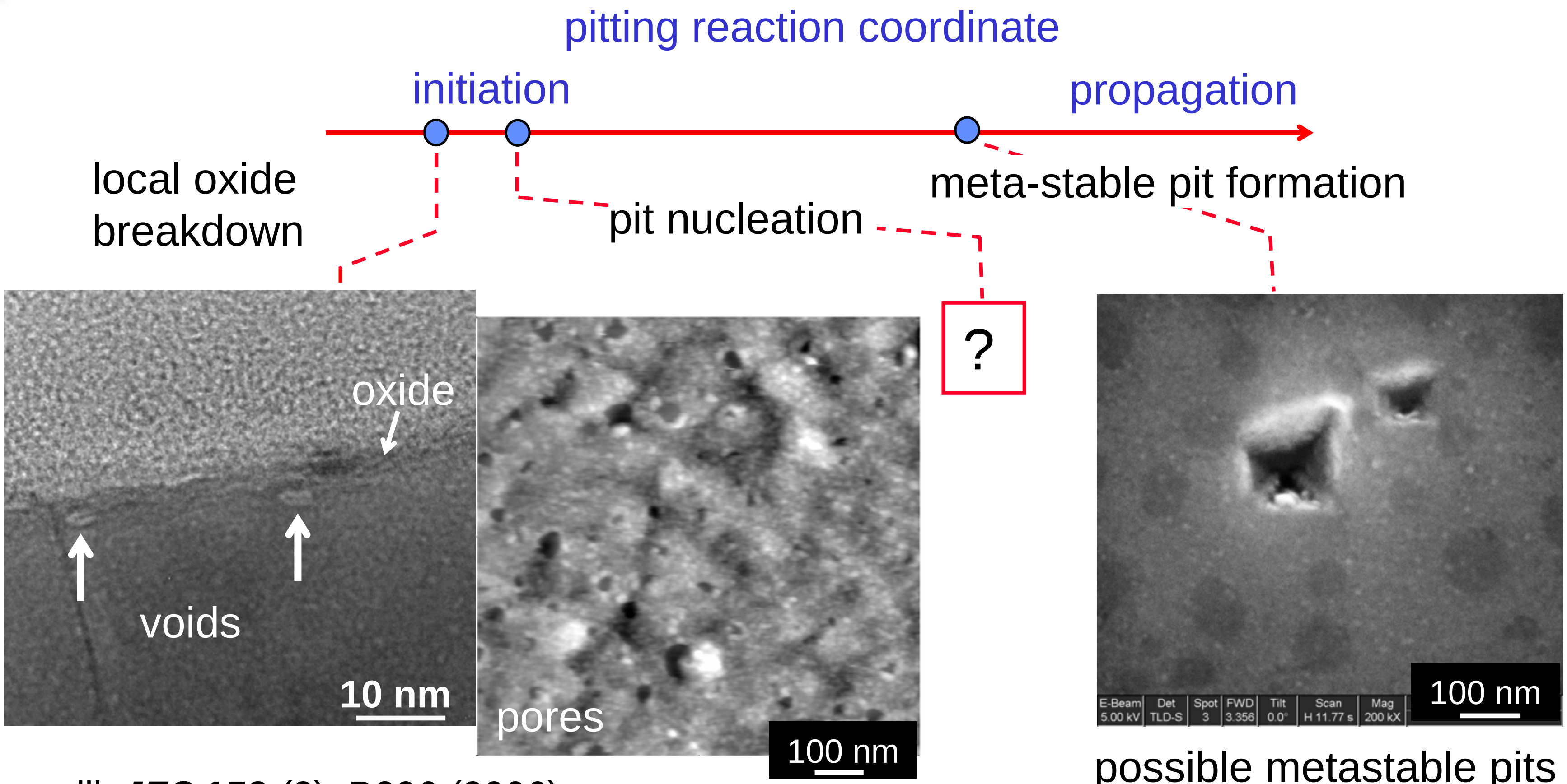


Can structure be guided at increasingly finer length scales during early stage growth?

Benefit: integrated optical or ultra capacitor based sensors

Our work contributes to the corrosion and nanosciences communities

Our goal is to identify relevant nanostructure and establish casual links with pit initiation



pitting reaction coordinate

initiation

propagation

local oxide breakdown

pit nucleation

meta-stable pit formation

?

Zavadil, *JES* **153** (8), B296 (2006)

possible metastable pits

sufficient chemical and physical descriptions do not exist for these entities

Model passive oxides on pure Aluminum are our starting point for initiation studies

Al single & polycrystals

vary oxide type:

O_2 derived

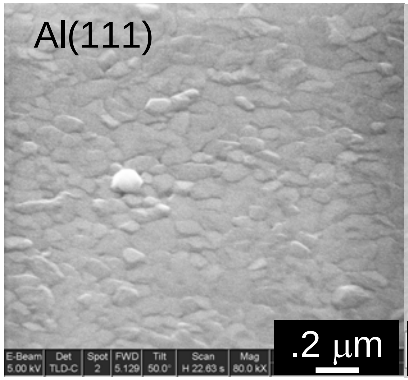
H_2O derived

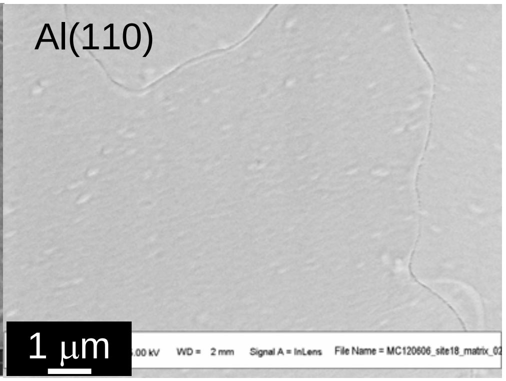
O derived – plasma

add markers:

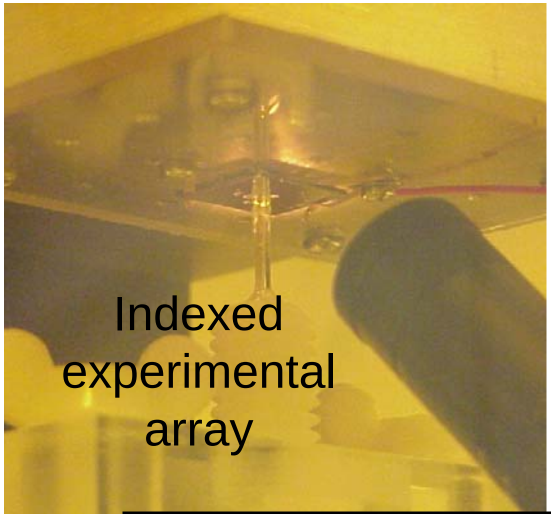
$^{18}O_2$

add microstructure





Capillary electrochemical systems* – statistical sampling



Probes:

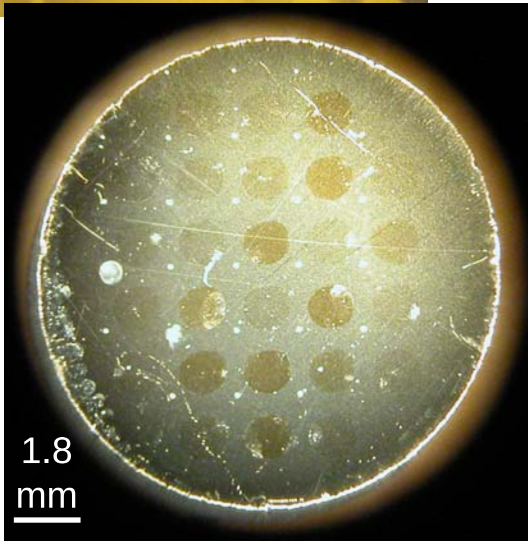
TOF-SIMS

TEM

FE-SEM

XPS

SPM



*developed through past LDRD and RF investments

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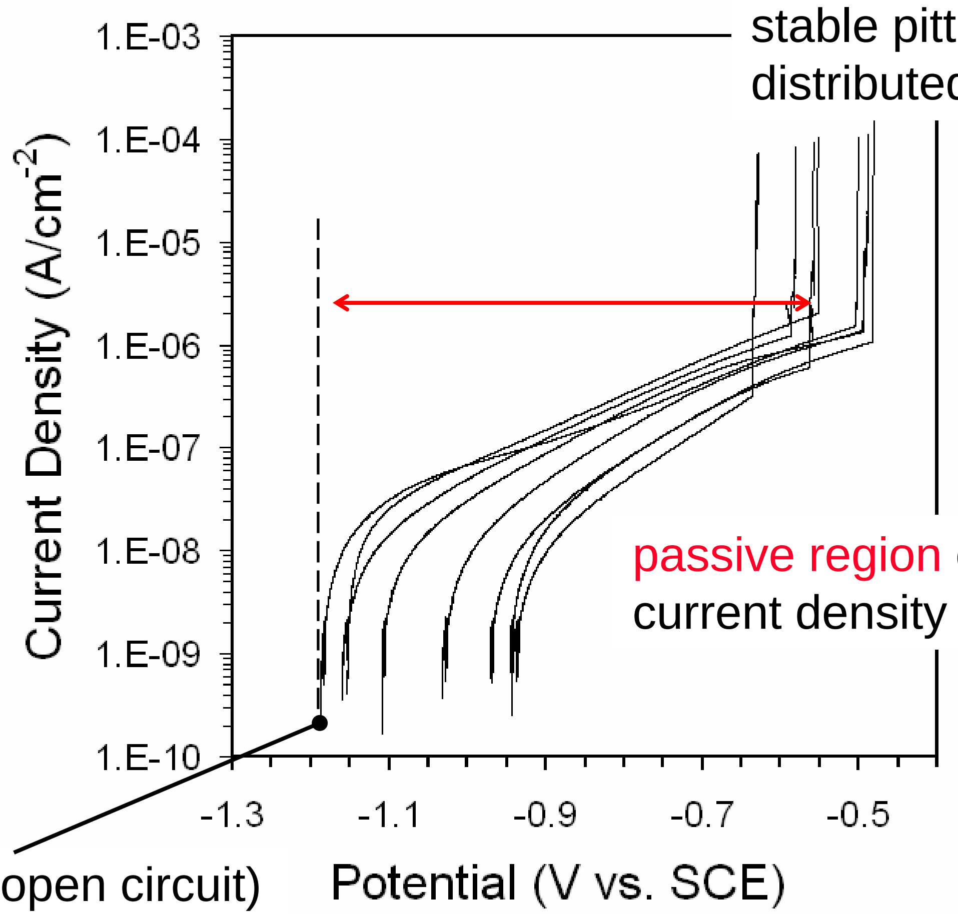
Potentiodynamic scans reveal variation in passive oxide response in advance of stable pitting

Al(110), 3 nm anhydrous oxide (O_2), equilibrated 12 hrs, 50 mM Cl^-



stable pitting is distributed in potential

passive region exhibits a variable current density – region of interest

equilibrium (open circuit) potential

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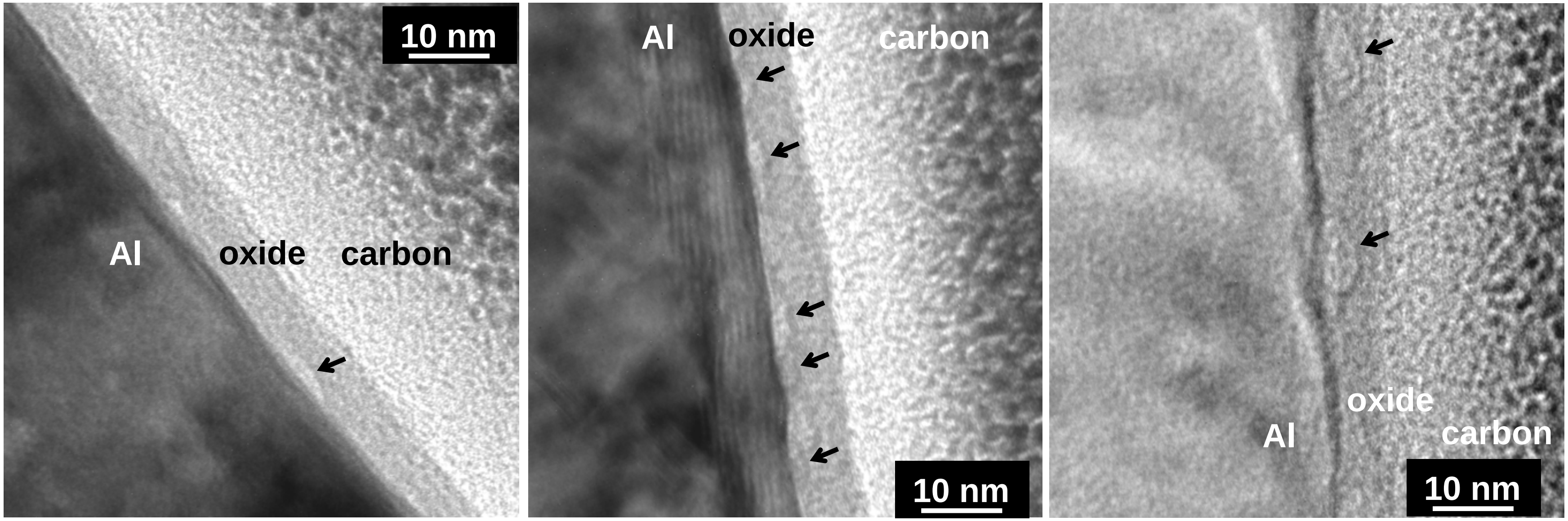
Nanoscale voids nucleate at the oxide:Al interface and grow into the oxide

O_2 formed oxide on Al(110)



14 hr OC

13 hr OC, -495 mV, 2.4 mC·cm^{-2}

4 hr OC, -518 mV, 4.2 mC·cm^{-2}

Increasing rate/extent of oxide growth

Void shape factor: oblate hemispherical shape ($d_{maj}:d_{min} \approx 2$) increased size with

no penetration of the substrate plane – the origin is the oxide

some alignment with substrate defect structure – nucleation sites

Zavadil, *JES* **153** (8), B296 (2006)

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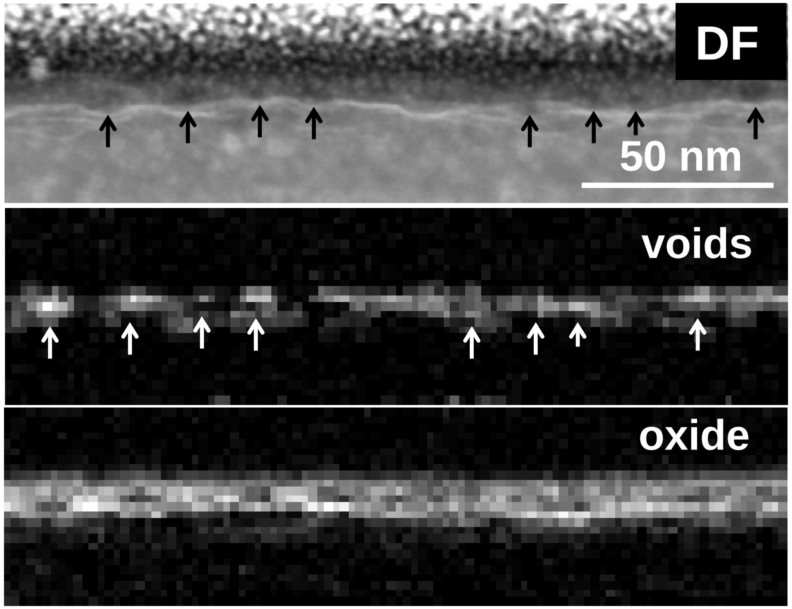
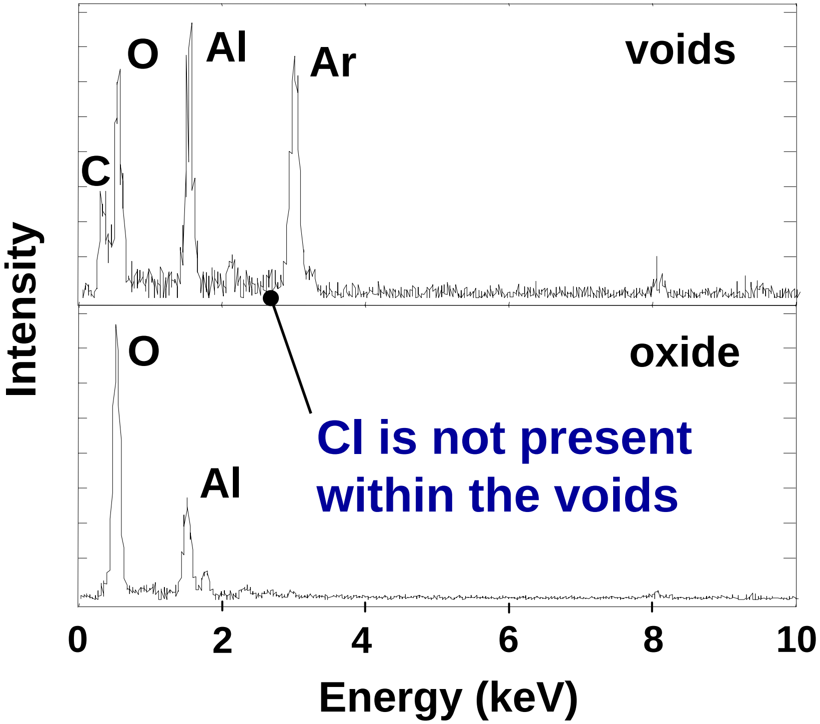
Analytical electron microscopy confirms the presence of voids



multivariate statistical analysis applied to EDS images



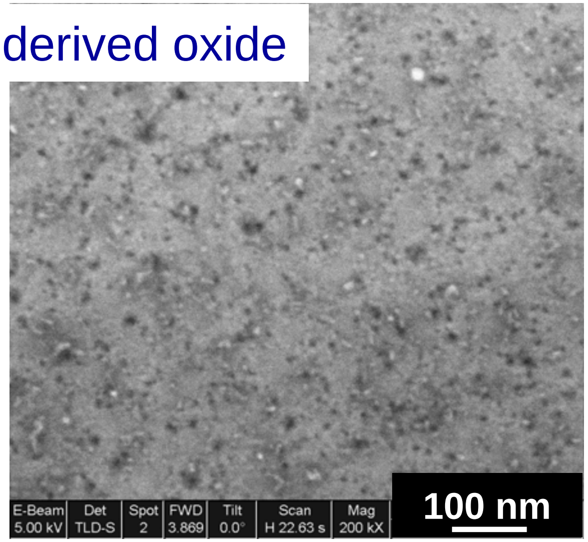
Cl is not present within the voids

Ar is not detected in thin films – fills voids after they form (Goodhew *J. Nucl. Mater.* 1988)

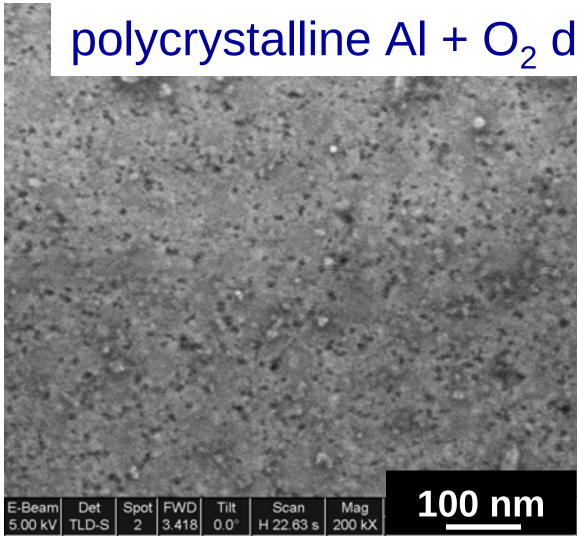
voids are consistent with a point defect mechanism for initial oxide modification as opposed to reagent penetration

Void formation appears generalized across a range of substrate microstructure and oxide types

Al(110) + O_2 derived oxide

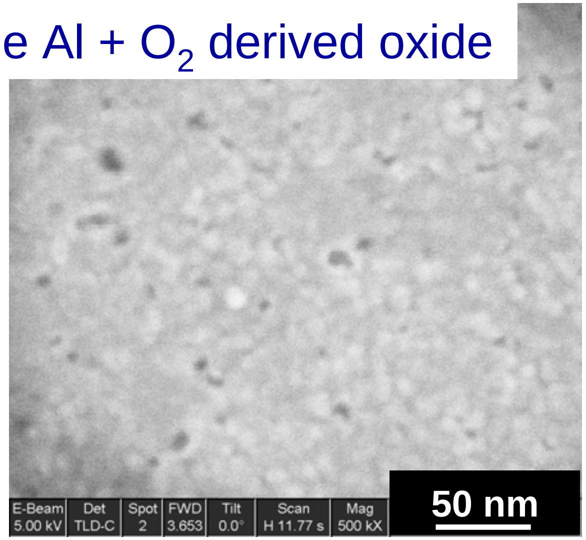


polycrystalline Al + O_2 derived oxide

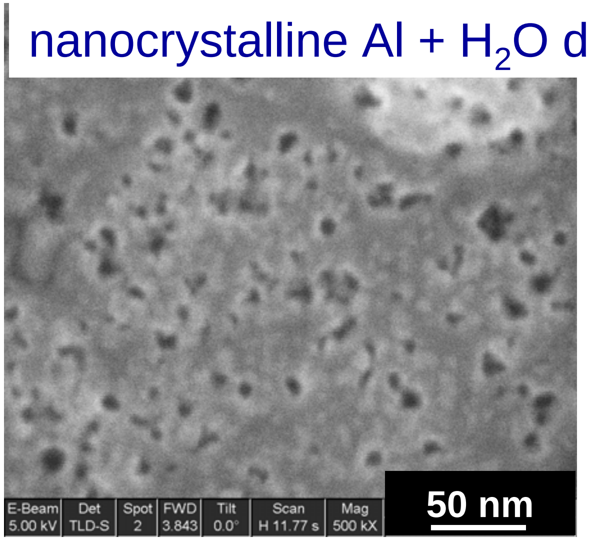


bulk

nanocrystalline Al + O_2 derived oxide



nanocrystalline Al + H_2O derived oxide



films

pores originate
as voids

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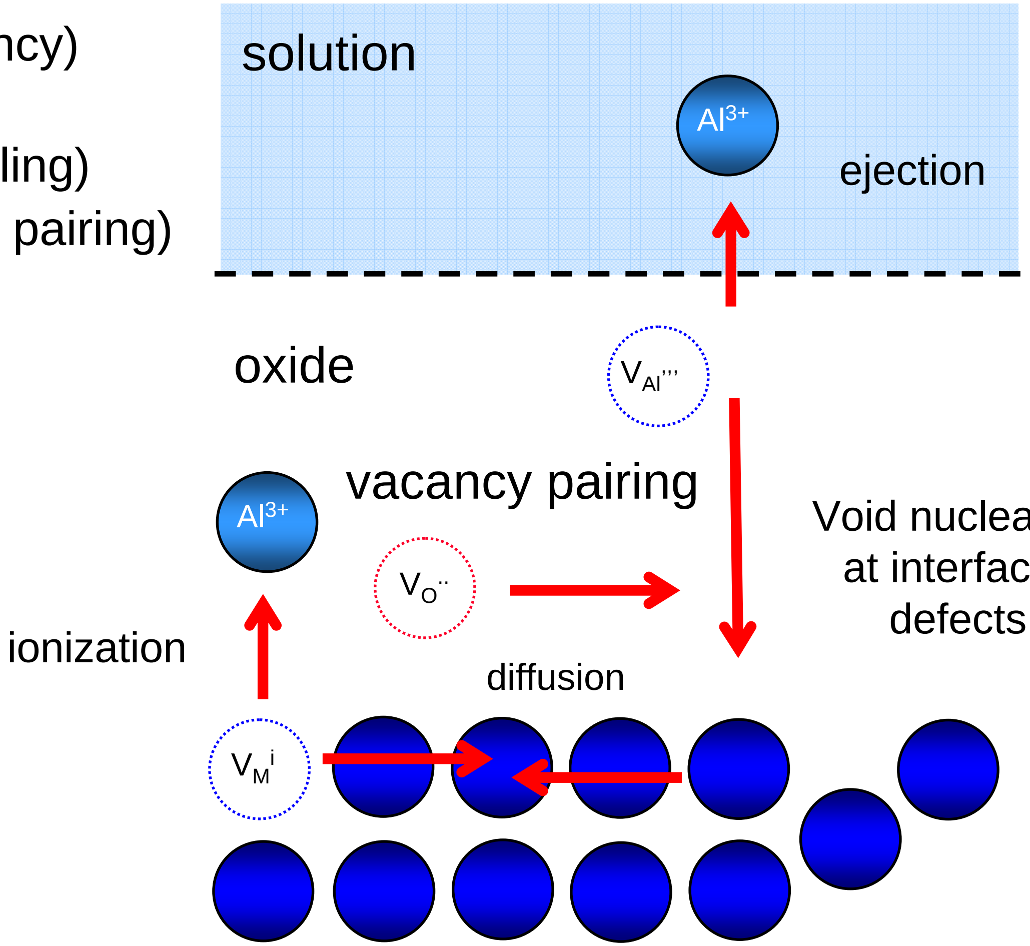
A vacancy pairing reaction produces void nucleation

parallel paths for ion (vacancy) transport :

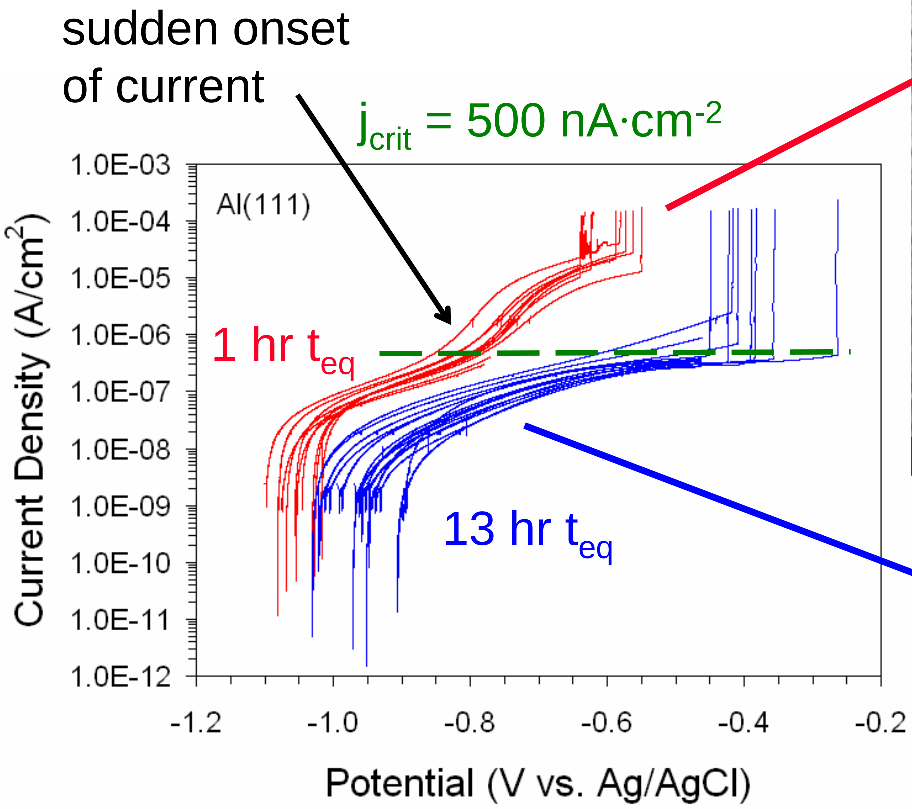
- oxide growth (vacancy filling)
- void nucleation (vacancy pairing)

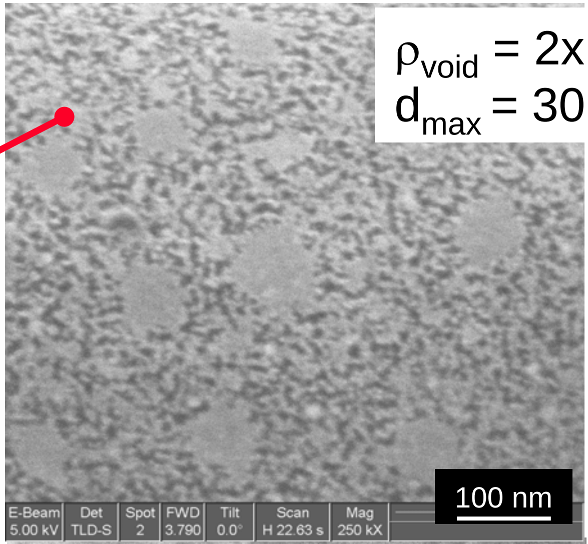
Factors that contribute to the site specificity of void nucleation:

- ionic conductivity of the oxide
- oxide:Al interfacial structure
- chemical composition at the oxide:electrolyte interface

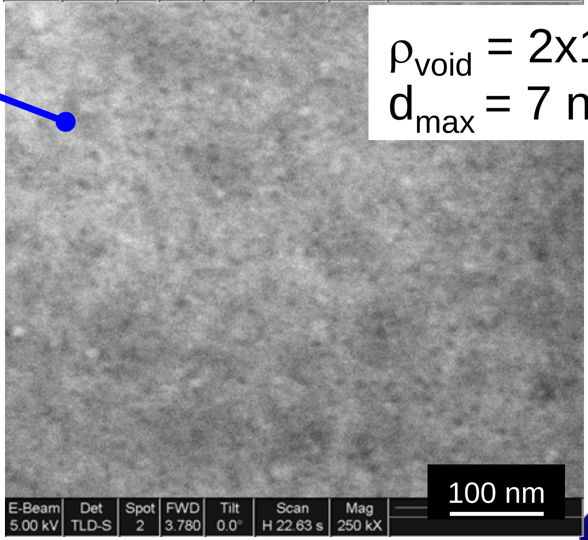


Stable pitting potential studies are not sufficient for establishing causal relationships





ρ_{void} = 2x10^{11} cm^{-2}
d_{max} = 30 nm



ρ_{void} = 2x10^{10} cm^{-2}
d_{max} = 7 nm

Void-to-pore transitions take place below the pitting potential – transition alone does not drive stable pitting

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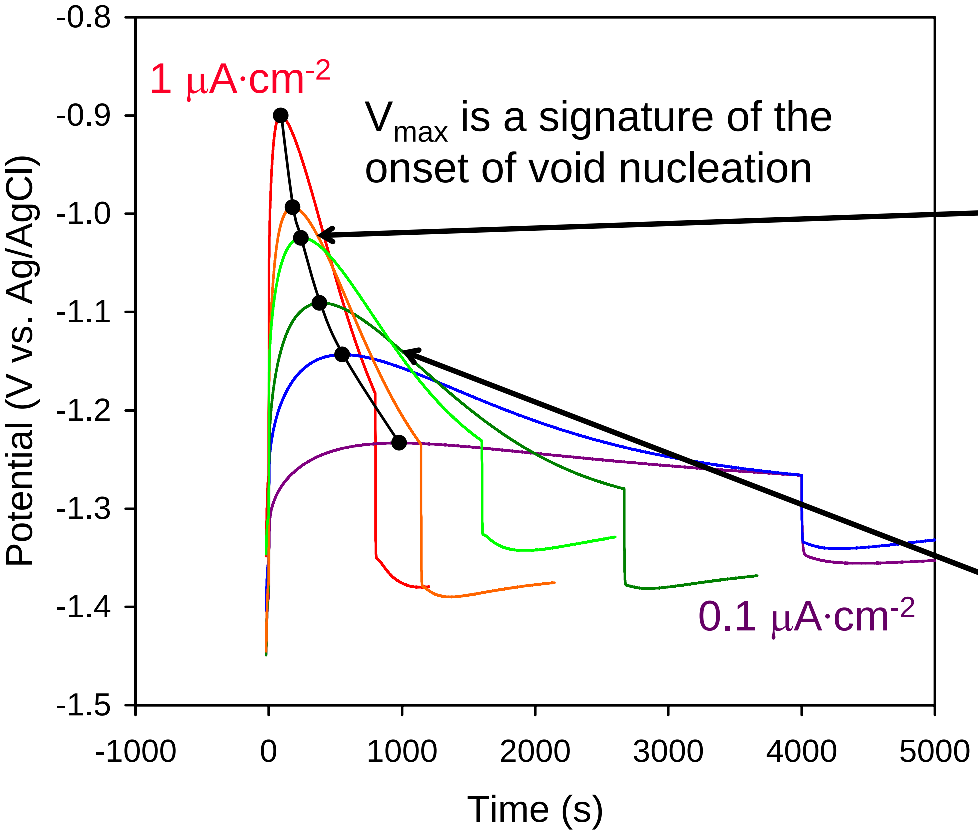
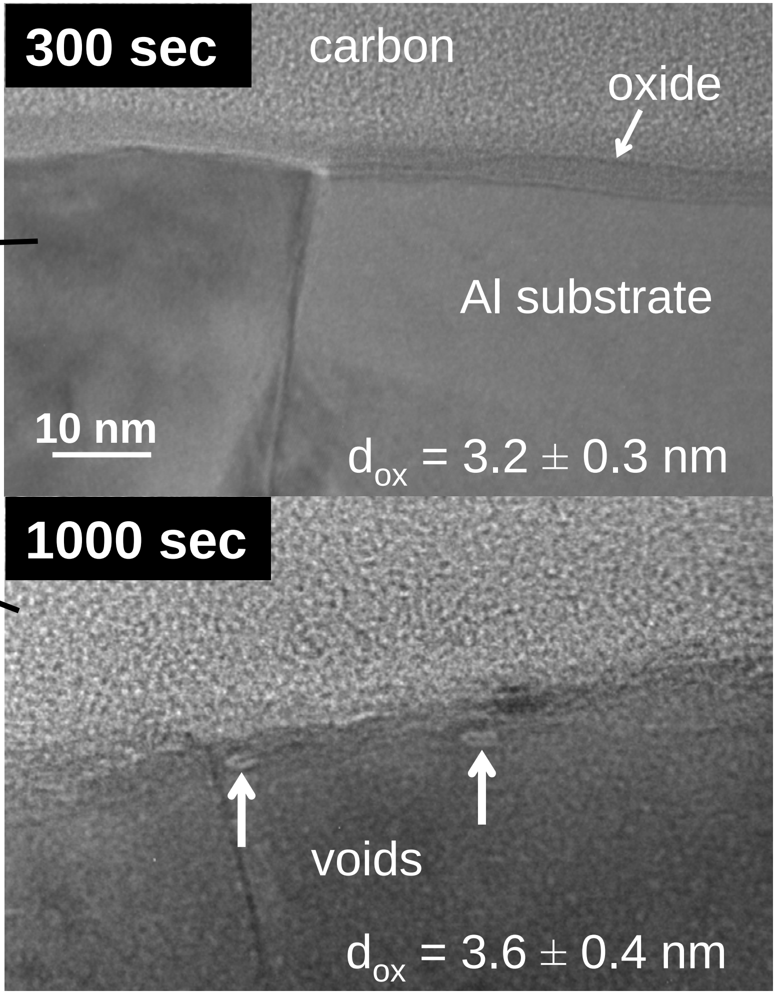
Voids can be generated by polarizing at constant anodic current densities



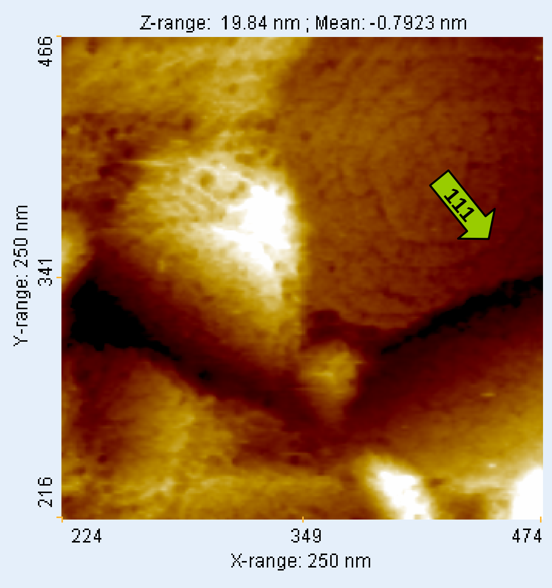
V_{max} is a signature of the onset of void nucleation

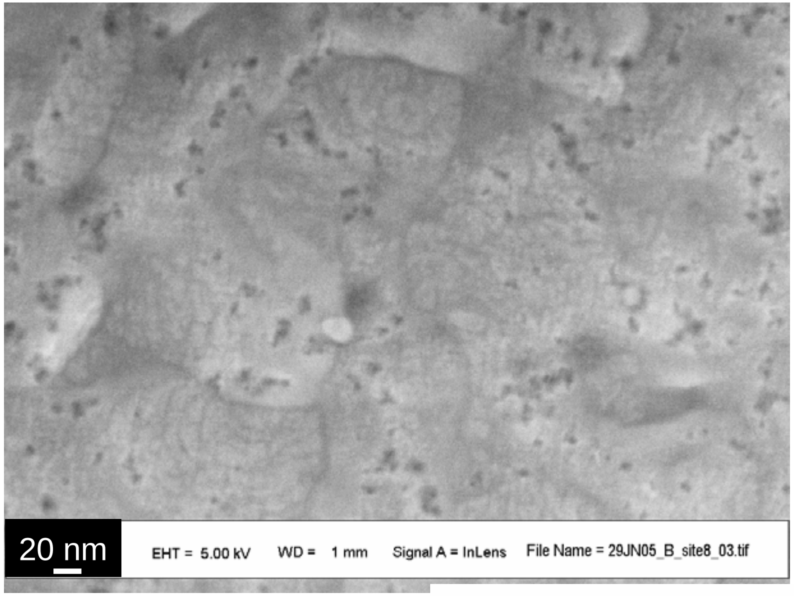


Controlling ionic flux and fluence can be used to tailor the void population

Zavadil *ECS Trans. 3* (2007) submitted

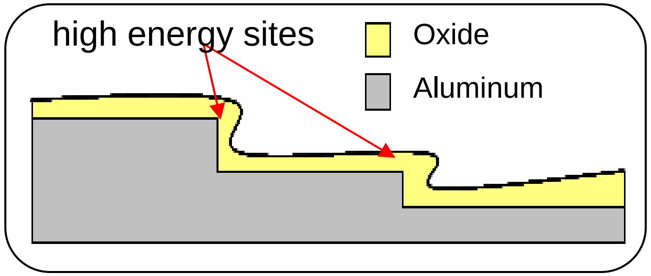
Voids nucleate at facet boundaries in nanocrystalline thin films





bulk	Al(111)	Al(110)
d_{ox}(anhydrous)	2.8 nm	3.2 nm
d_{ox}(equilibrated)	3.9 nm	4.9 nm
R_{ox}(equilibrated)	$8\text{x}10^6\ \Omega\cdot\text{cm}^2$	$4\text{x}10^6\ \Omega\cdot\text{cm}^2$
films		
d_{ox}(anhydrous)	2.9 nm	--------
d_{ox}(equilibrated)	3.9 nm	--------
R_{ox}(equilibrated)	$5\text{x}10^6\ \Omega\cdot\text{cm}^2$	$3\text{x}10^6\ \Omega\cdot\text{cm}^2$

hybrid resistivity



Rapidly expanded oxide at step edges may be most susceptible

Edges as effective vacancy trap sites

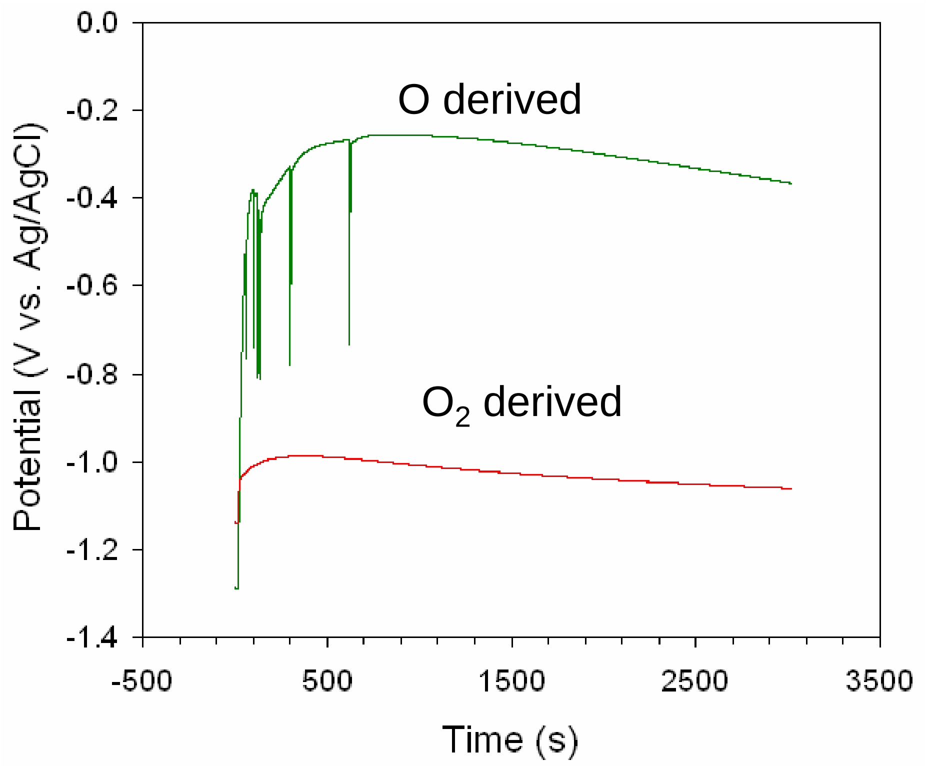
Zavadil *ECS Trans.* 1(4) 139 (2006)

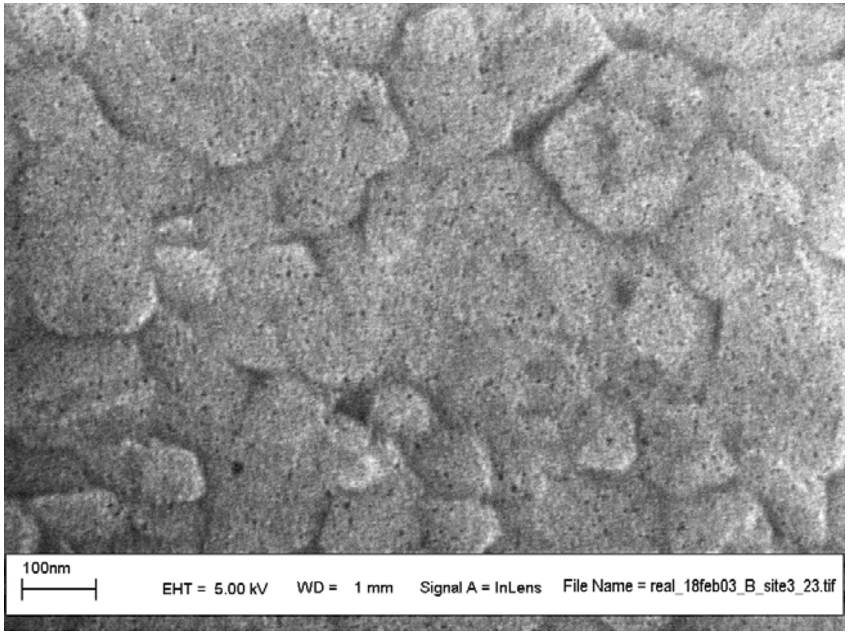
Zavadil, MS&T Jan07

Decreasing the ionic conductivity of the oxide results in spatially random void nucleation

an attempt at decoupling the oxide properties from oxide:Al interfacial structure

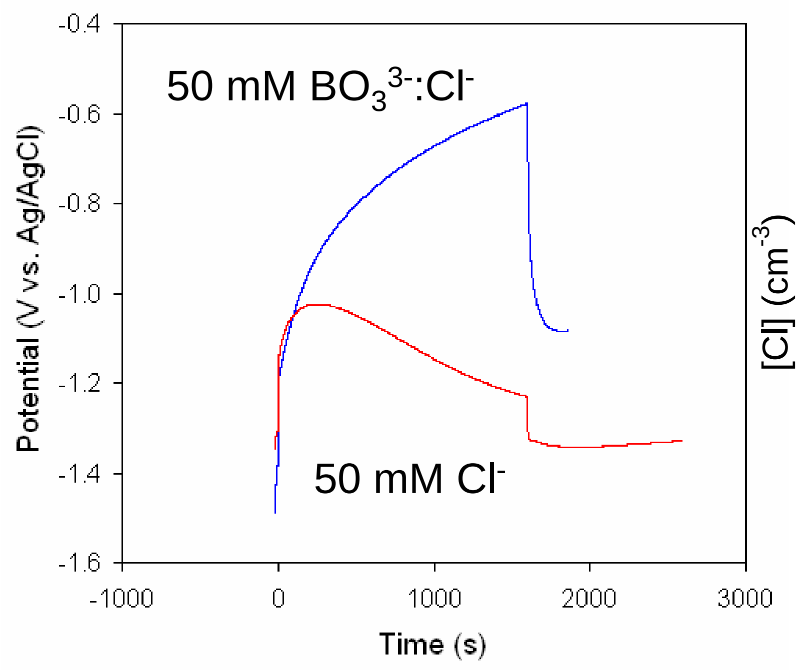
O derived (plasma) oxide on Al(111): d_{ox} = 4.5 nm, R_{ox} = 7×10^{6} $\Omega \cdot cm^{-2}$

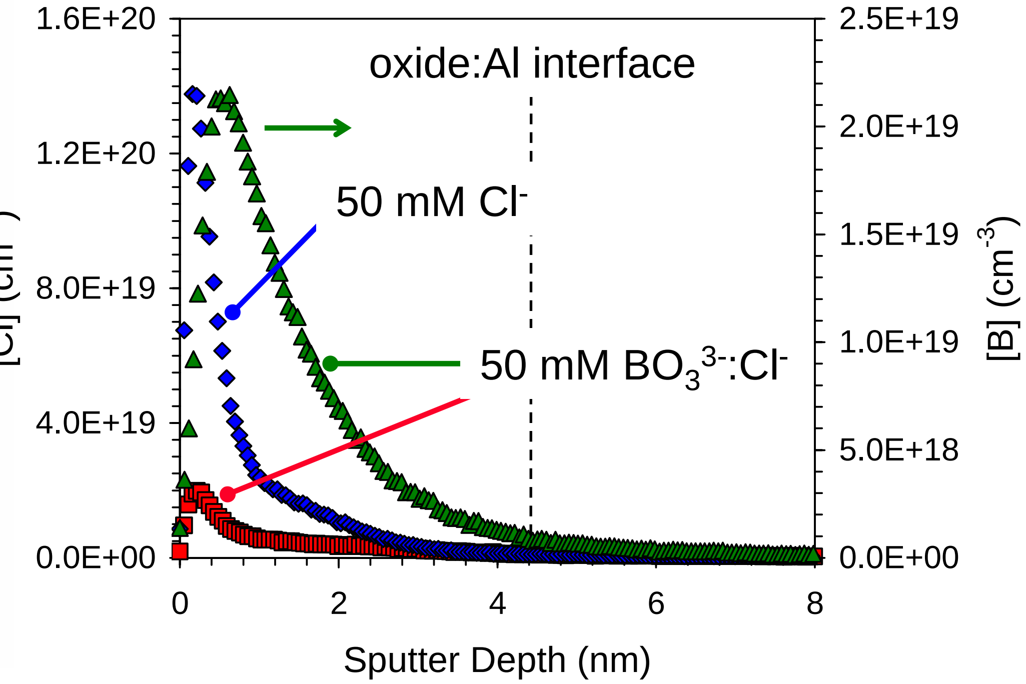




Local variations in oxide conductivity appear to be the more dominant driver for where void nucleate and grow

Chloride acts to catalyze the ejection of the aluminum cation





oxide growth is more dominant with borate present

10X decrease in [Cl^-] due to BO_3^{3-} competitive adsorption

Electrolyte	**Void Density (cm^{-2})**	**Void Diameter (nm)**
chloride	8×10^{10}	4 - 9
chloride:borate	8×10^{9}	8 - 16
borate	2×10^{9}	8 - 16

borate regulates Al^{3+} ejection

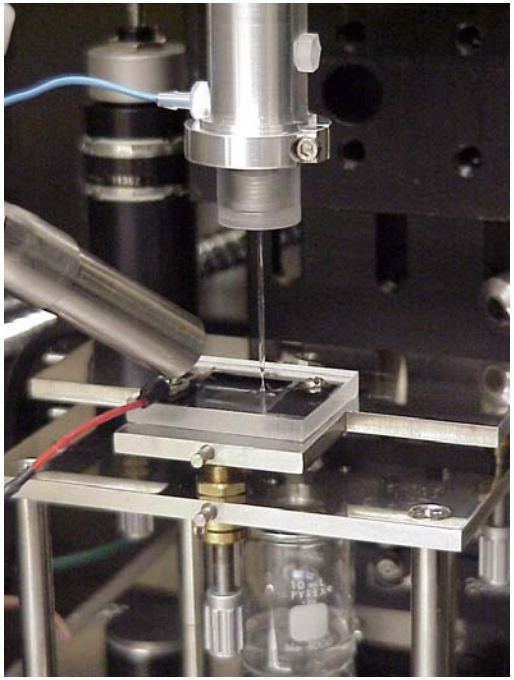
Zavadil *JES* (2007) submitted.

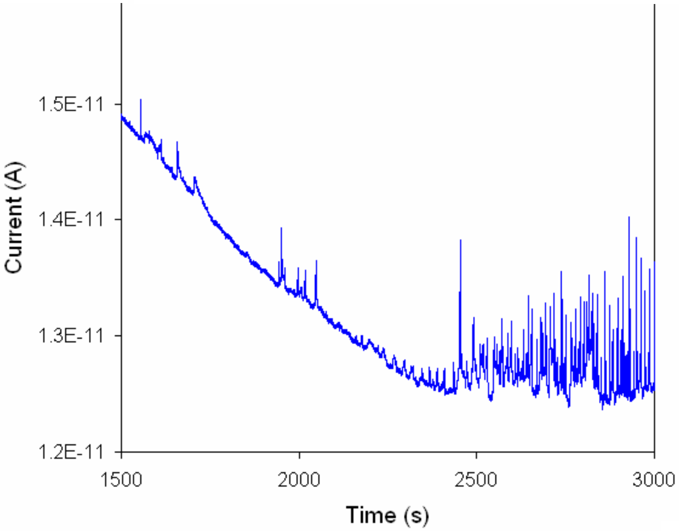
Zavadil, MS&T Jan07

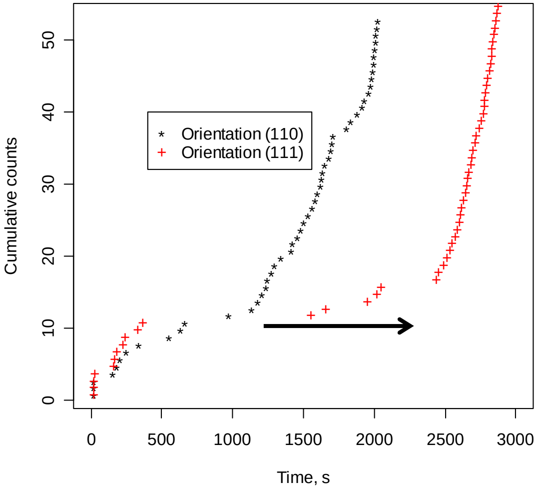
Pit nucleation event detection is one approach to correlate voids with pit initiation

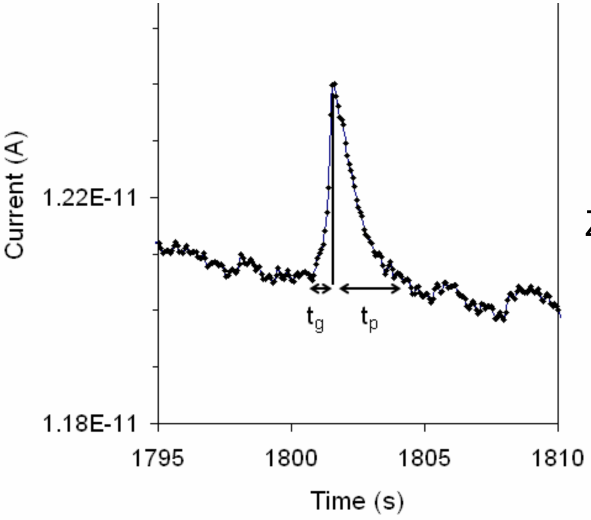
void population is programmed

pit nucleation events are probed & characterized









oxide - driven difference in induction time for the larger pit nucleation events

assume that the probabilities of pit nucleation and metastable pit frequency can be related

Zavadil *ECS Trans.* 3 (2007) submitted.

Collaboration with Industrial Research Ltd., NZ

Sandia National Laboratories

Zavadil, MS&T Jan07

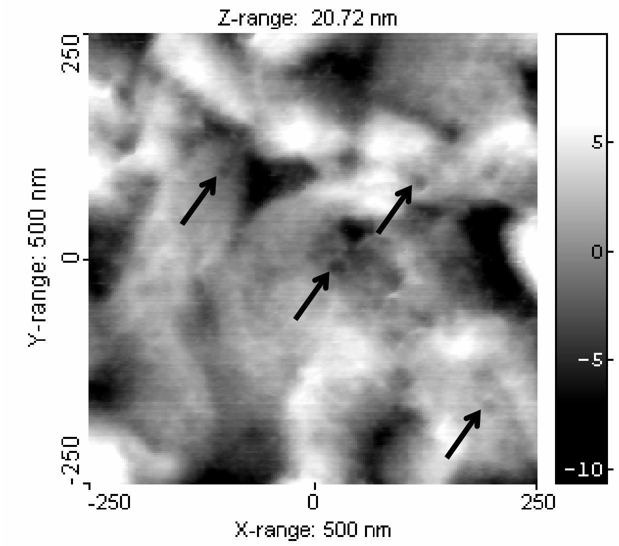
Nanostructure characterization must accompany these statistical studies

attempting to account for localized contributions to anodic current

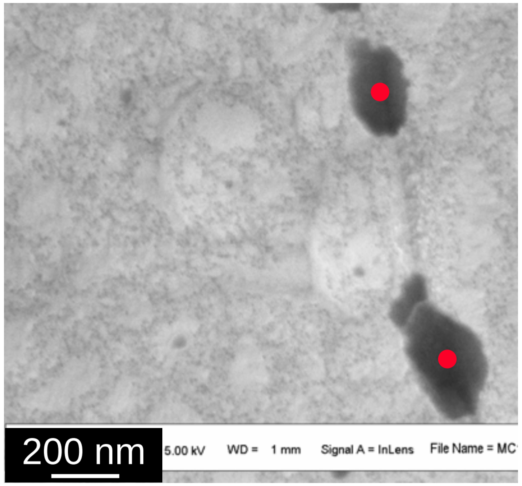
event tracking – structural features that exhibit a size increment with time

secondary goal – define the physical scale of pit nuclei and metastable pits

30 to 50 μm diameter μcapillaries make SEM and AFM imaging manageable



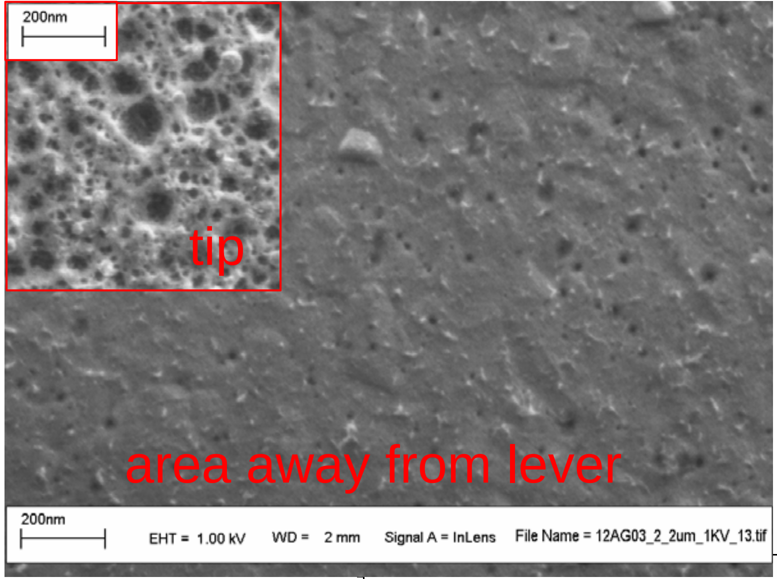
void-to-pore transition on Al(111)

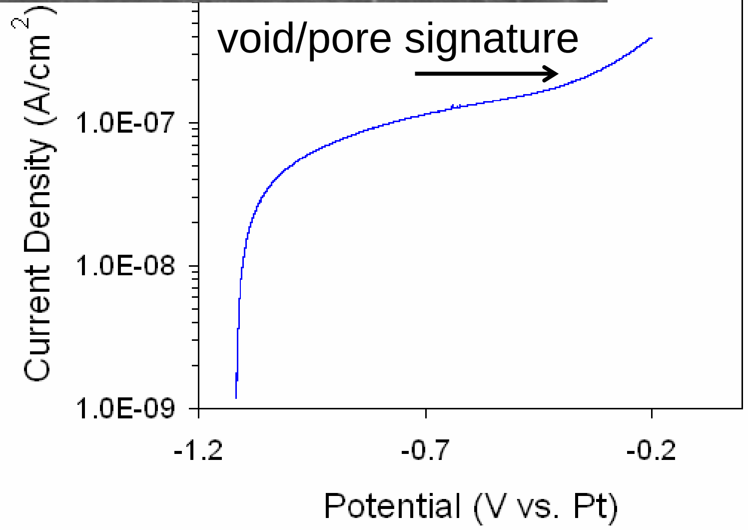


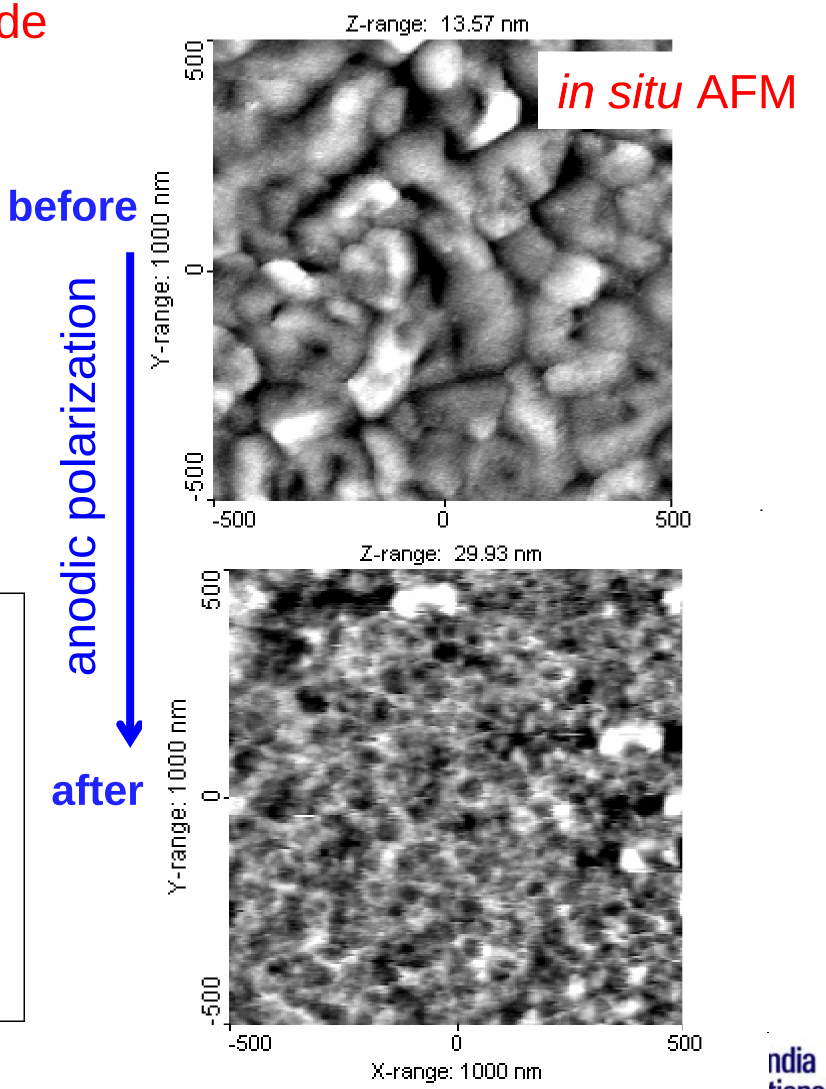
anodic dissolution features on Al(110) do not produce current transients

In situ methods appear promising for locally inducing and imaging oxide breakdown

Pt-coated cantilever as a counter electrode






in situ AFM

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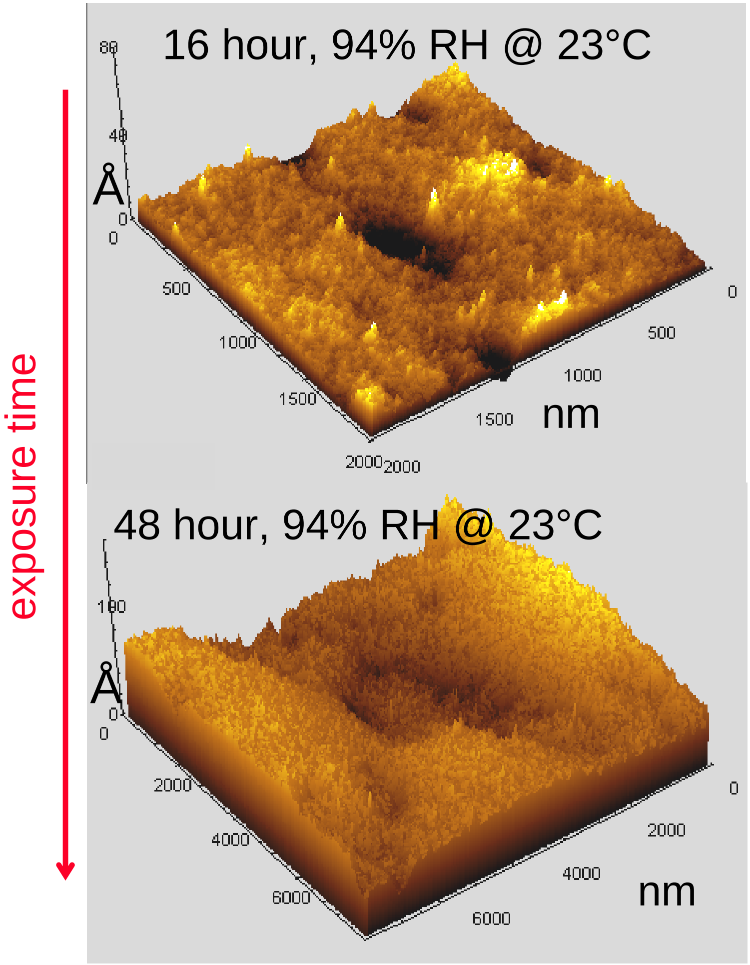
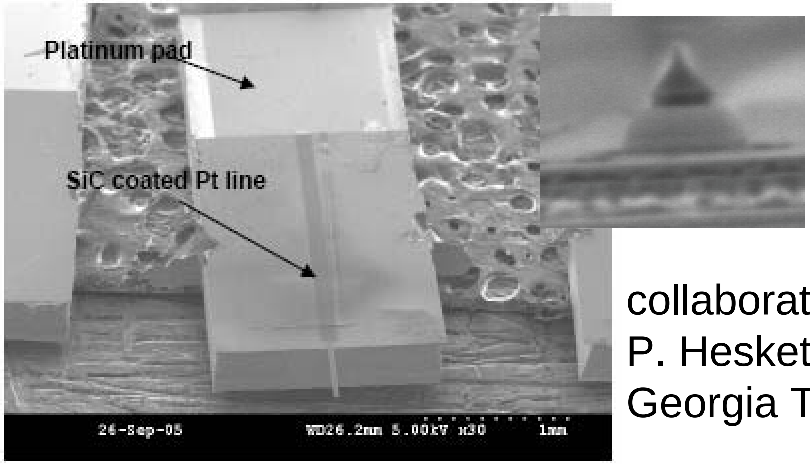
Initiation studies in low dimensional water films are used to study atmospheric corrosion

Tungsten corrosion



additional electrochemical characterization can be implemented – scanning electrochemical microscopy on an AFM



collaboration -
P. Hesketh,
Georgia Tech.

This approach can be applied to study initiation site susceptibility in corrosion resistant, engineered barrier materials – C22 alloy (Ni-Cr-Mo) for Yucca Mountain repository

Summary of Accomplishments

- First identification of interfacial void formation for Al under typical polarization conditions
- Galvanostatic techniques shown to yield signatures for void nucleation
- Demonstrated that site specificity for void formation is controlled by oxide ionic conductivity
- Evidence provided for the catalytic role of chloride in facilitating the ejection of Al cations into solution in void nucleation
- Demonstrated an ability to electrochemically tailor a void population
- Pit nucleation event measurement and characterization demonstrated
- Demonstrated novel *in situ* methods for inducing and tracking oxide breakdown

Our mechanistic understanding and methods impact Sandia’s predictive capability

- A nanoscale breakdown process that can be related to oxide properties and possibly pit nucleation is identified and described

- These correlations are the first step in mapping a complex degradation path that culminates in accumulated damage responsible for material function loss

- Continued effort in mapping this pathway will provide additional critical details for predicative model input:

  sources of pit nucleation site specificity

  physical and compositional descriptors for high probability initiation-to-propagation events

- Our overall approach, knowledge and tools are applicable to other nanoscale, stochastic phenomena

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