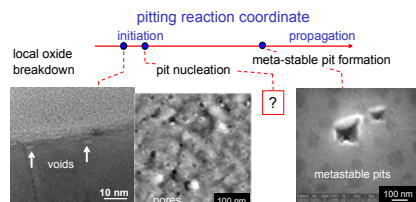


Mapping a Pitting Reaction Coordinate



Zavdil et al. *JES* **153** (8), B296 (2006)

Nanostructure has historically been invoked to explain why passivity loss is localized and leads to pit initiation in passive metals

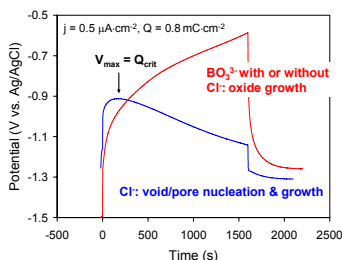
Materials reliability models require:

- sufficient chemical and physical descriptions of nanostructural entities
- establishment of these entities as causal agents for pit initiation

Mechanism of Nanostructure Formation

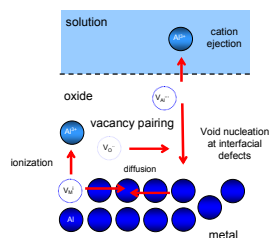
Applied anodic current (Al oxidation) produces two processes:

- oxide growth – vacancy filling
- interfacial void nucleation and growth – vacancy pairing

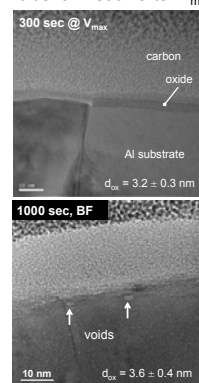


- Shape of the curve is a signature for dominant void nucleation & growth
- Q_{crit} is a measure of the void nucleation efficiency

vacancy filling vs. pairing reactions



voids form soon after V_{max}



a lower density of voids are detected with BO_3^{3-} and dominant oxide growth

Electrolyte composition dictates whether void formation is the dominant process

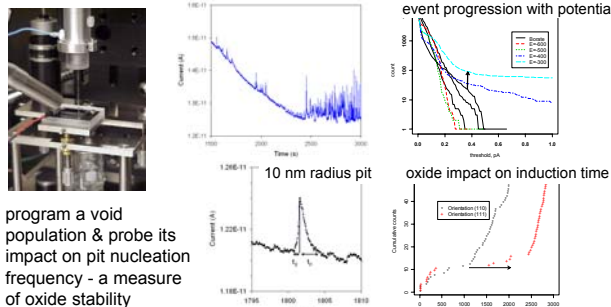
Factors:

- constituent regulated defects that alter vacancy mobility
- adsorbates that facilitate cation ejection

Knowledge of the void formation mechanism can be exploited to control the location, size & density of voids and resulting pores

Establishing Causality – Voids as Pit Precursors

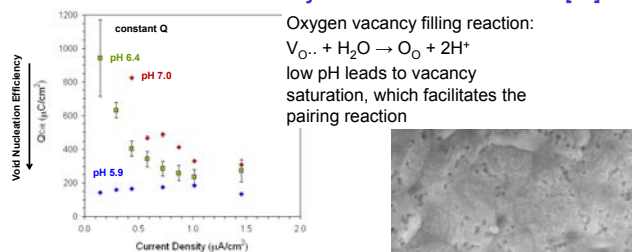
Pit nucleation event detection as a method for correlating the presence of voids with pit initiation



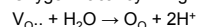
program a void population & probe its impact on pit nucleation frequency - a measure of oxide stability

collaboration with J. Soltis & D. Krouse, IRL, NZ

Void nucleation efficiency increases with increased [H⁺]



Oxygen vacancy filling reaction:



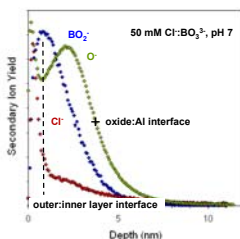
low pH leads to vacancy saturation, which facilitates the pairing reaction

pH	Density (cm^{-2})	Mean Diameter (nm)	Maximum Diameter (nm)
5.9	8×10^{10}	5	< 12
6.4	4×10^{10}	4	< 10
7.0	8×10^9	10	> 10

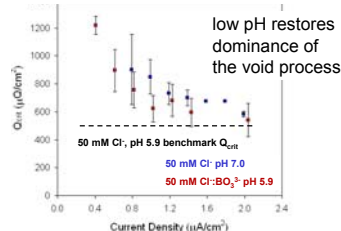
void nucleation location is correlated with structure and/or oxide properties

Competitive anion adsorption

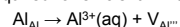
BO_3^{3-} (+ polyborate anions) displaces Cl⁻ at an outer hydrous layer – inner barrier layer interface



Q_{crit} (mc/cm^2)	d_{ox} (nm)	pH	$[BO_3^{3-}]$ (mM)	$[Cl^-]$ (cm^{-3})	$[BO_2^-]$ (cm^{-3})
0	2.9	7	0	1.0×10^{20}	9.1×10^{18}
0	3.5	7	5	1.1×10^{20}	8.0×10^{18}
0	2.9	7	50	3.3×10^{19}	1.2×10^{19}
1.6	3.5	7	0	2.3×10^{20}	1.3×10^{19}
1.6	4.0	7	5	1.5×10^{20}	1.2×10^{19}
1.6	3.9	7	50	2.9×10^{19}	2.0×10^{19}
1.6	3.6	5.9	0	2.4×10^{20}	5.6×10^{18}
1.6	3.5	5.9	50	7.8×10^{19}	3.9×10^{19}



Sufficient Cl⁻ is required for efficient Al vacancy generation:



Inducing & Imaging Localized Passivity Breakdown

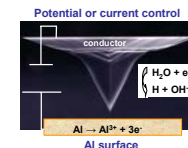
Localize electrochemical stress to define event location

Combine AFM with electrochemical machining (Schuster & Ertl, Science 2000)

point-and-polarize – short times localize field and constrain location

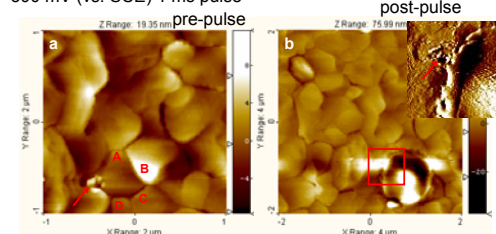
$$t = C_1 \cdot \rho_{soln} \cdot d$$

μm resolution at 10^1 ns pulses widths



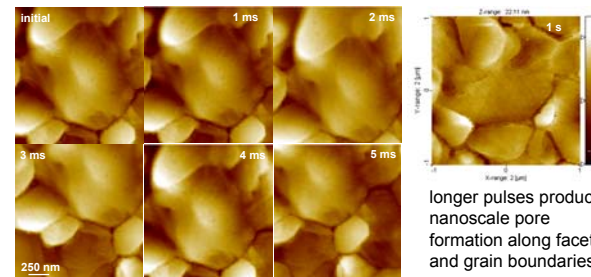
Pitting can be driven in proximity to a conductive tip

-300 mV (vs. SCE) 1 ms pulse



A degree of reproducibility is demonstrated for pit proximity to tip location
Potential method for pit susceptibility mapping

In situ tracking of oxide structural changes



longer pulses produce nanoscale pore formation along facet and grain boundaries

short pulses produce a transition from aligned platelets along growth steps to a more nodular structure – oxide growth and step edge disruption with O²⁻ incorporation

Future Work:

- Develop and exploit fast pulse (10 nsec) capability in EM-AFM experiment to conduct breakdown susceptibility mapping
- Correlate void nucleation location with oxide:metal interface structural motifs as directed by first principles calculations
- Statistically correlate void population characteristics with pit nucleation frequency
- Develop and apply spectroscopic STM to explore the nanocrystalline oxides on passive transition metals

*Localized Corrosion Project Team: N.A. Missert, P.J.

Feibelman, P.G. Kotula, & N. Vasiljevic. Thank you G. Copeland and J. Stevens of Sandia National Labs for Al thin film deposition, B. McKenzie for SEM, & J.A. Ohlhausen for TOF-SIMS. Work sponsored by DOE Basic Energy Sciences Division of Materials Science & Engineering