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Inducing and Imaging Localized Passivity Breakdown in Aluminum using an AFM Approach

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DOE Basic Energy Sciences Office of Materials & Engineering Sciences

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

pitting reaction coordinate

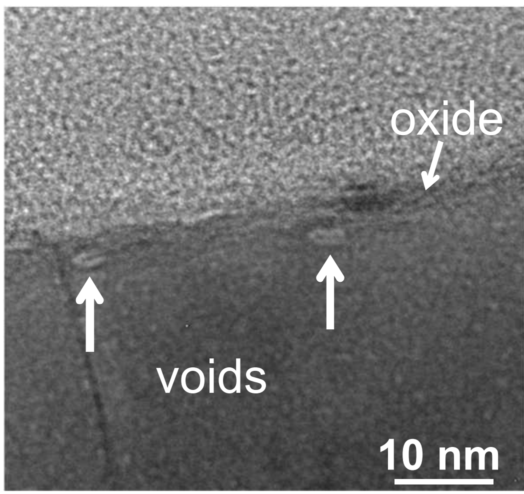
initiation — propagation

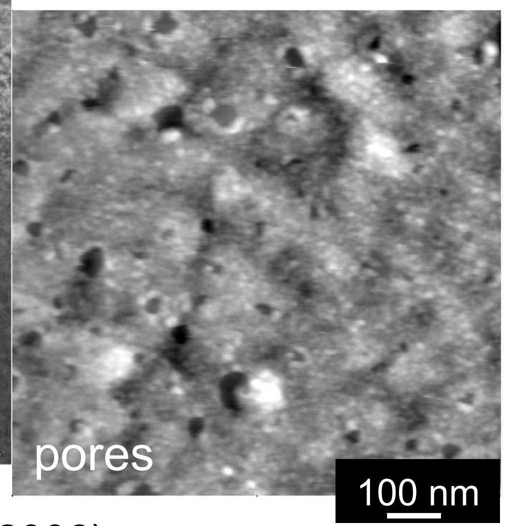
local oxide breakdown

pit nucleation

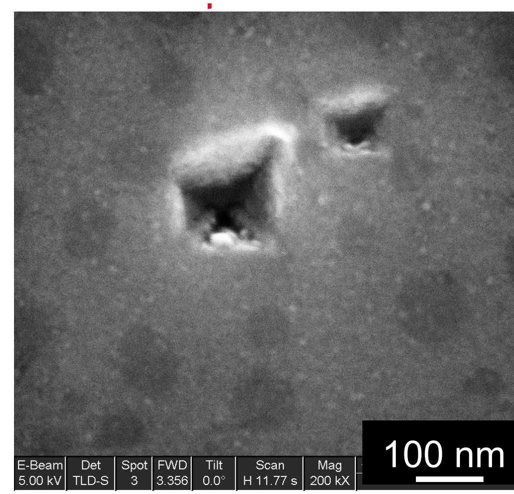
meta-stable pit formation

?





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



possible metastable pits

sufficient chemical and physical descriptions do not exist for these entities to support reliability models for high consequence applications of passive metals

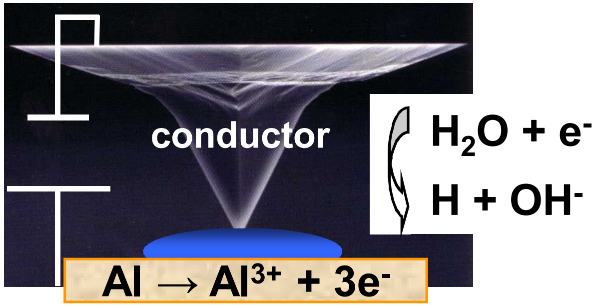
AFM-based approach for inducing local passivity loss

Building from the electrochemical machining field (Schuster & Ertl, Science 2000, Hudson)

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

  μm resolution at 10^1 ns pulses widths
- local current density can be achieved to match metastable pit requirements (10^4 $A \cdot cm^{-2}$)

Potential or current control



Al surface

Proof of concept studies relax the time constraint – msec to sec pulse widths

Operate at 400 nm tip-surface separation

Al thin films are used to facilitate AFM imaging

Type 1:

Al thin films electron beam deposited onto SiO_2:Si

Nanocrystalline Al(111) textured films are formed - grain dia. 100 to 150 nm

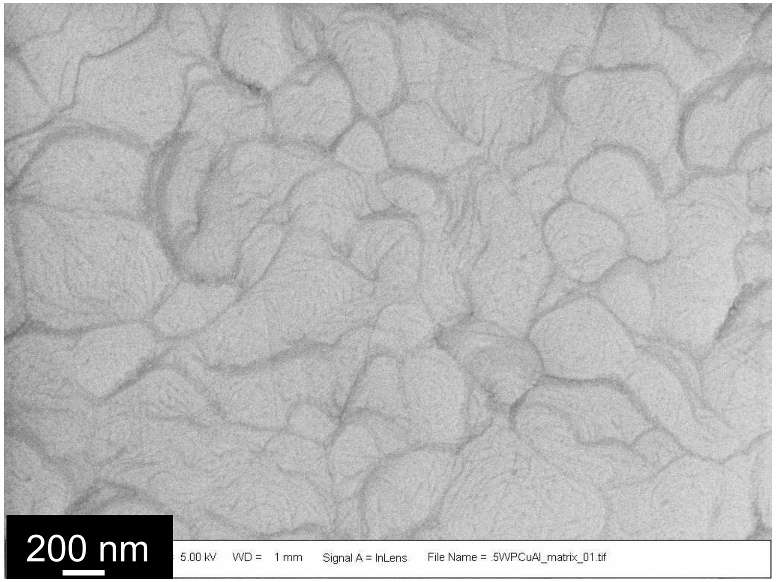
Anhydrous oxides O_2 grown immediately after film deposition

Type 2:

Al-0.5 wt% Cu thin films sputter deposited onto TiN:Ti layer on Si – CMOS interconnect technology

Al(111) texture films are formed - grain dia. 200 to > 500 nm

Air formed oxide at room temperature



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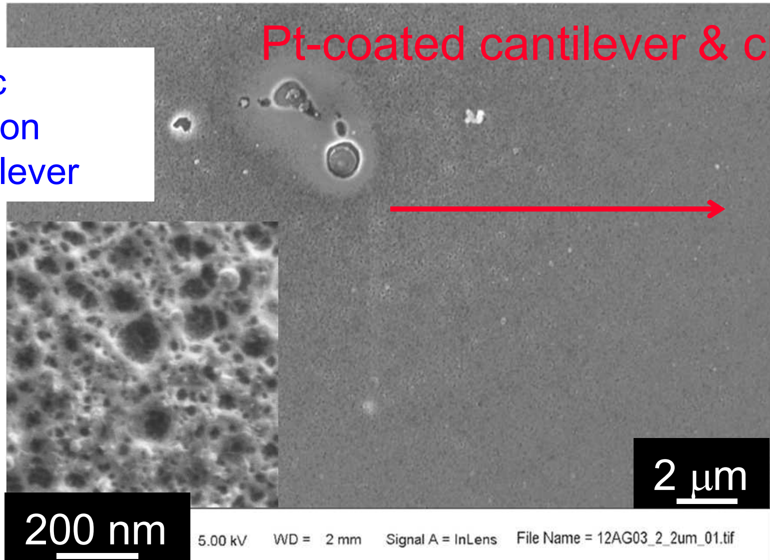
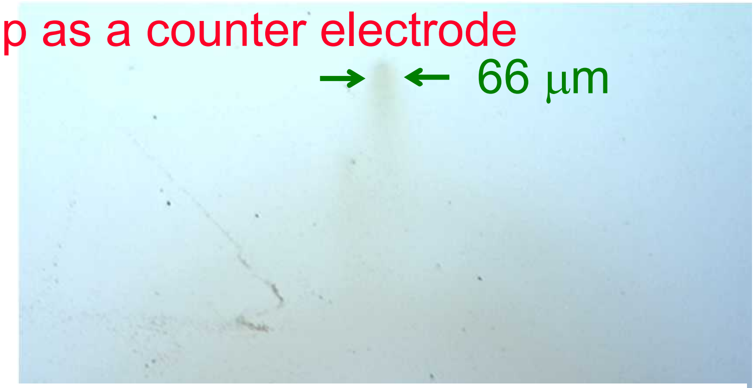
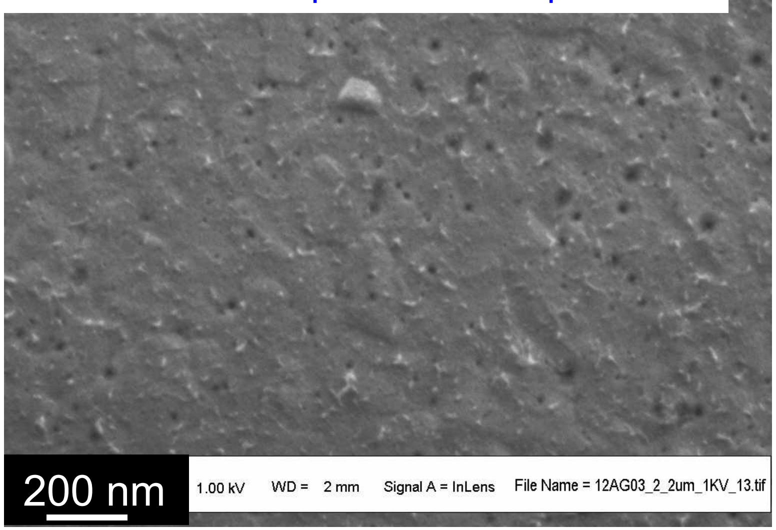
Initial attempts focused on sweeping the potential of the lever & chip to evaluate localization

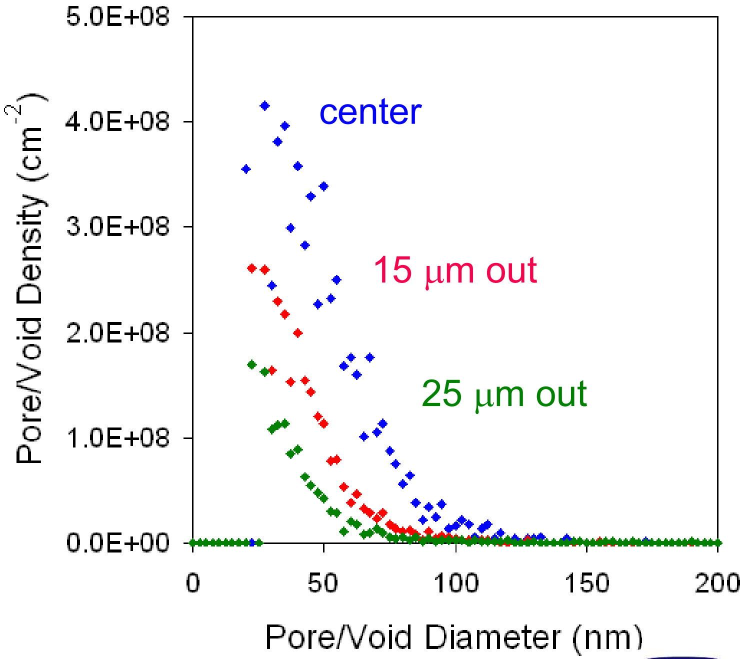
Anodic oxidation under lever



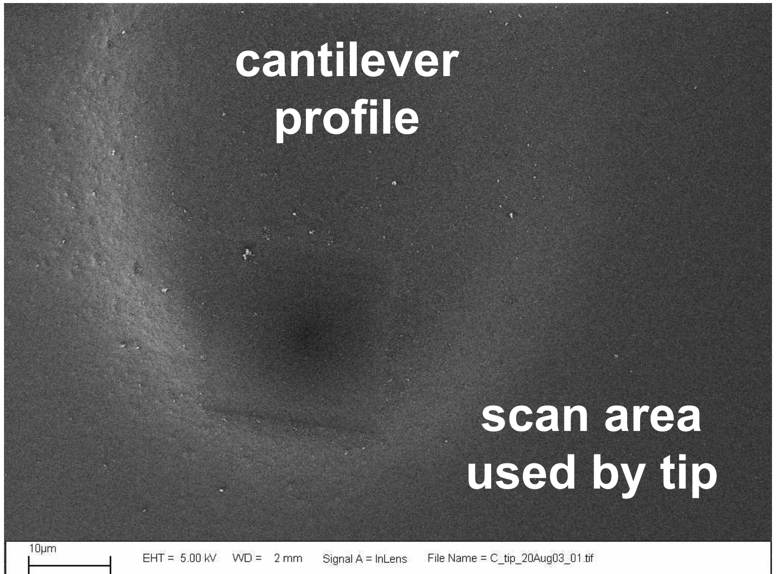


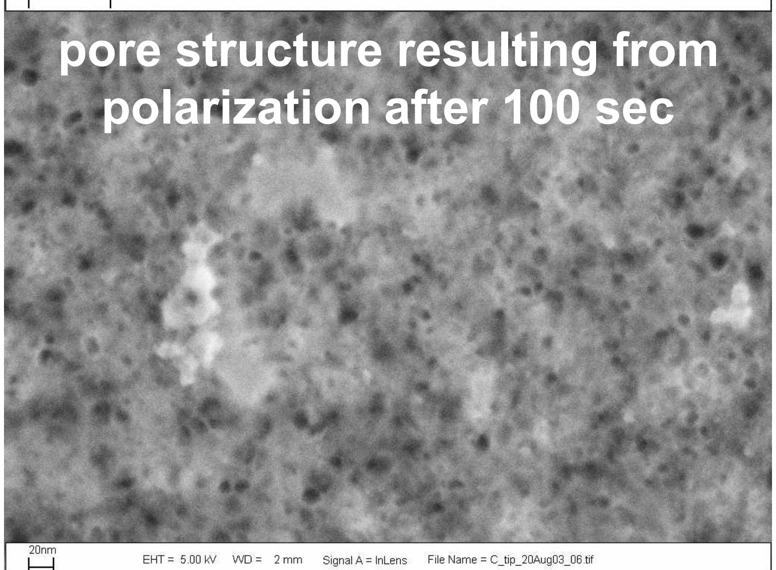
Transition to nano-pores at lever perimeter



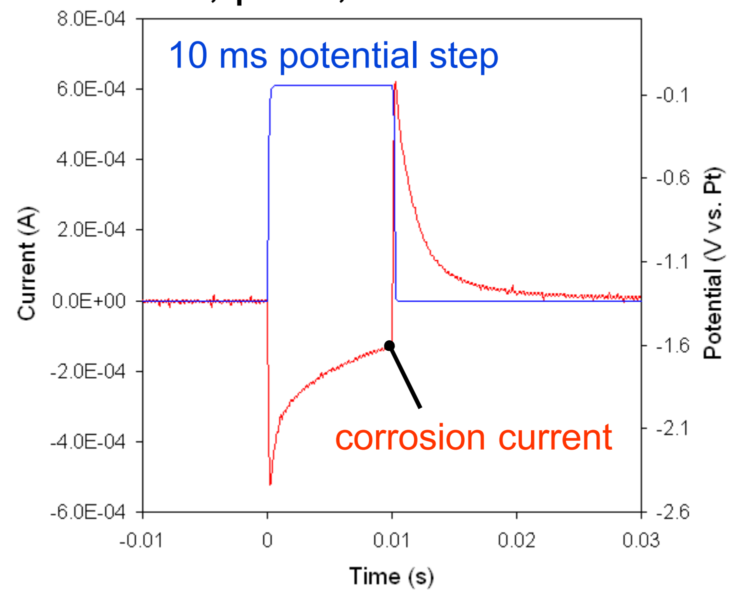


Electrical insulation of the chip and holder assembly further improves localized response





50 mM Cl^-, pH 7, contact mode



Anodic activity can be localized to the tip and lever perimeter

We do not drive pitting at 0V for pulse times up to 100 sec – consistent with void formation in this system

Limited by imaging mode and details of tip-surface interactions within this materials system

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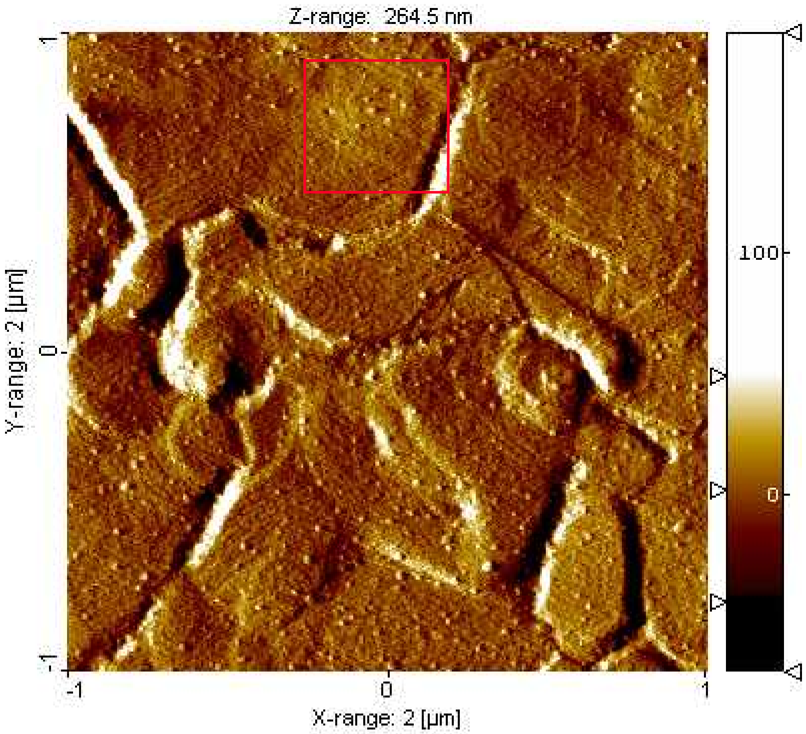
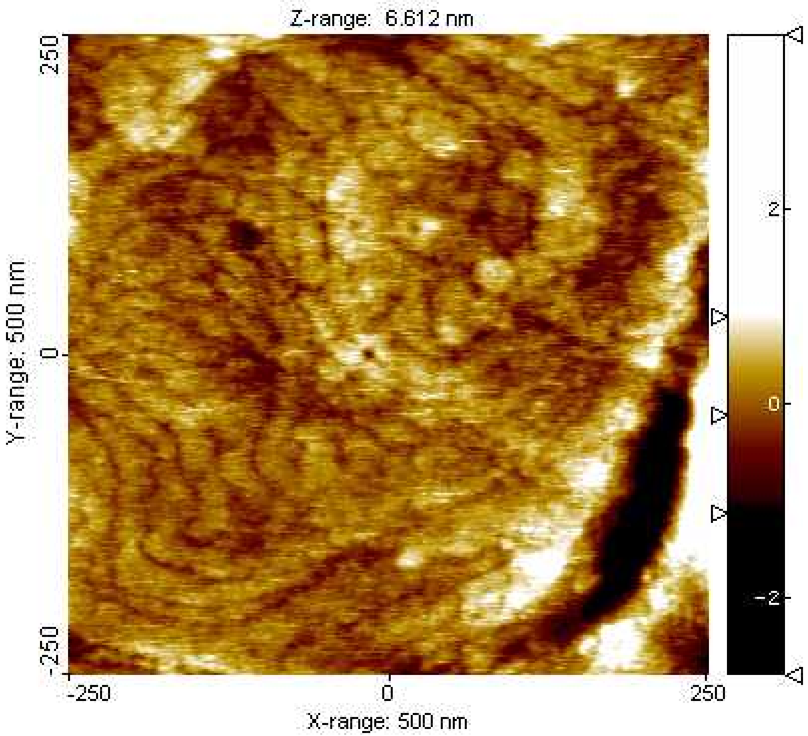
Imaging fidelity improves markedly on going to AM-AFM in an attractive mode

hydrated Al - 0.5 wt% Cu film in 50 mM Cl^-, pH5.9



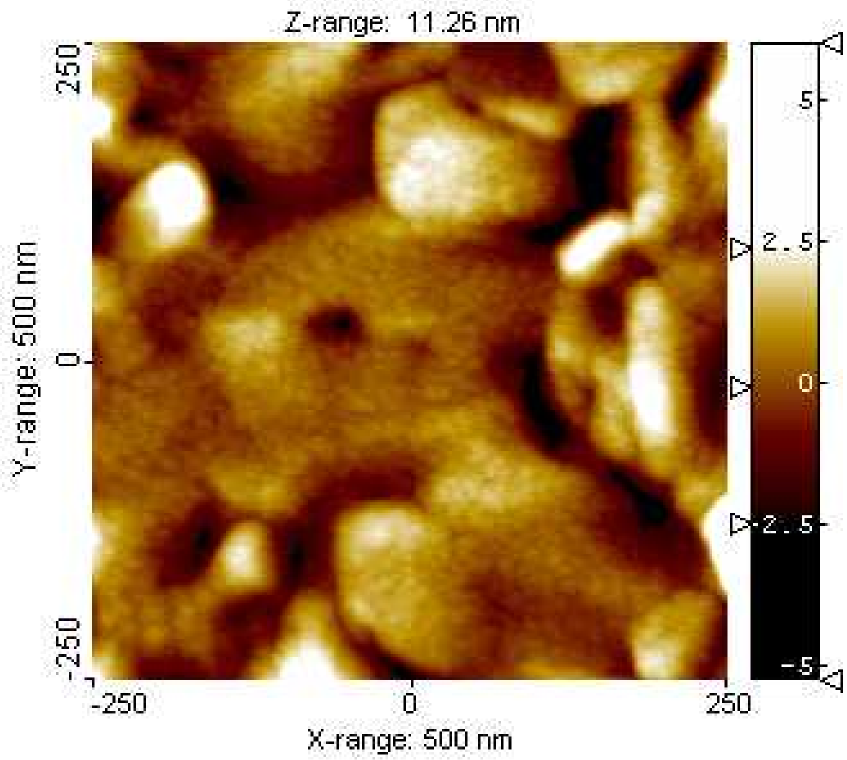
growth steps from the deposition process are evident

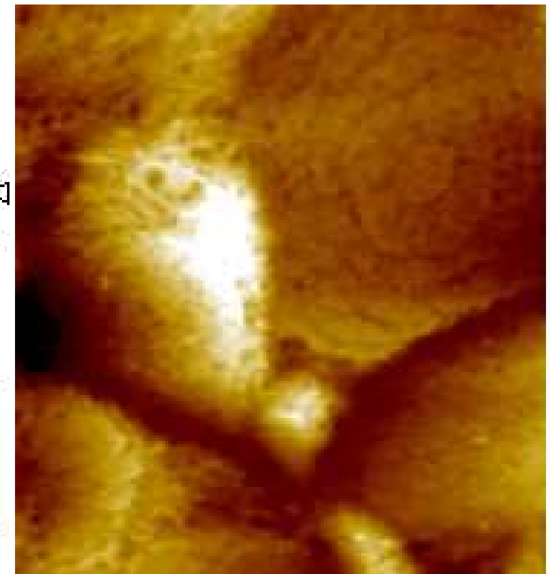


oxide platelets decorate the growth step edges

Structure is consistent with previous imaging of dry and hydrated surfaces

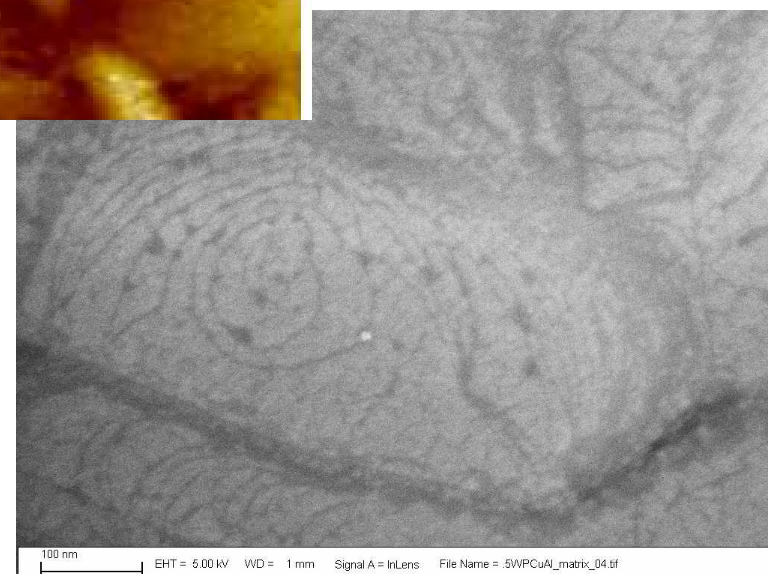
Type 1 Al films





imaging improves in H_2O (1x1 μm^2)

platelets with discontinuities



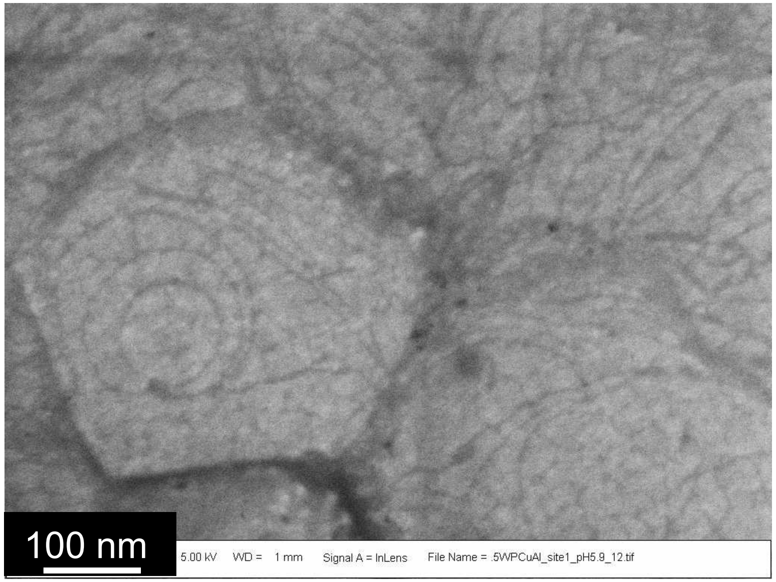
attractive mode imaging in N_2 shows morphological structure to the oxide

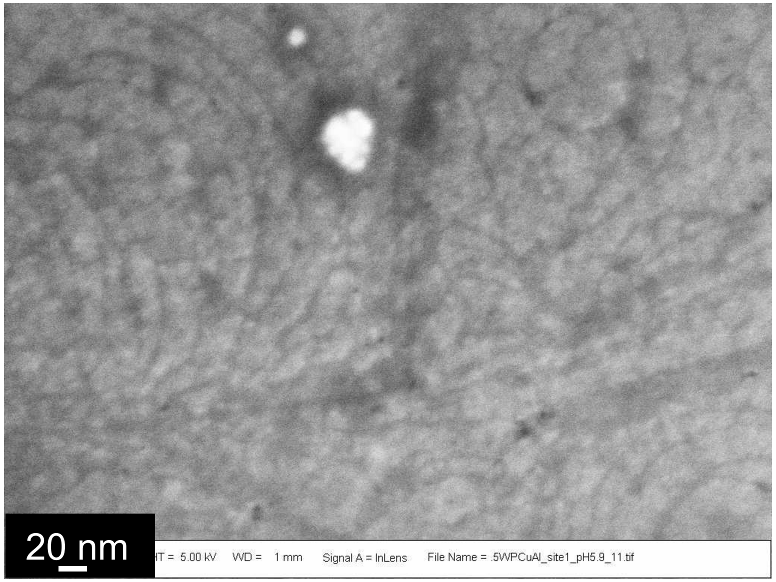
Type 2 Al-Cu films

We anticipate nanopores will form in the Al-0.5 wt% Cu system with polarization

Slow rate polarization of Al-0.5 wt% Cu in 50 mM Cl-, pH 5.9 at 167 $\mu V \cdot s^{-1}$

ex situ SEM





a fine pore structure appears at facet perimeters and grain boundaries

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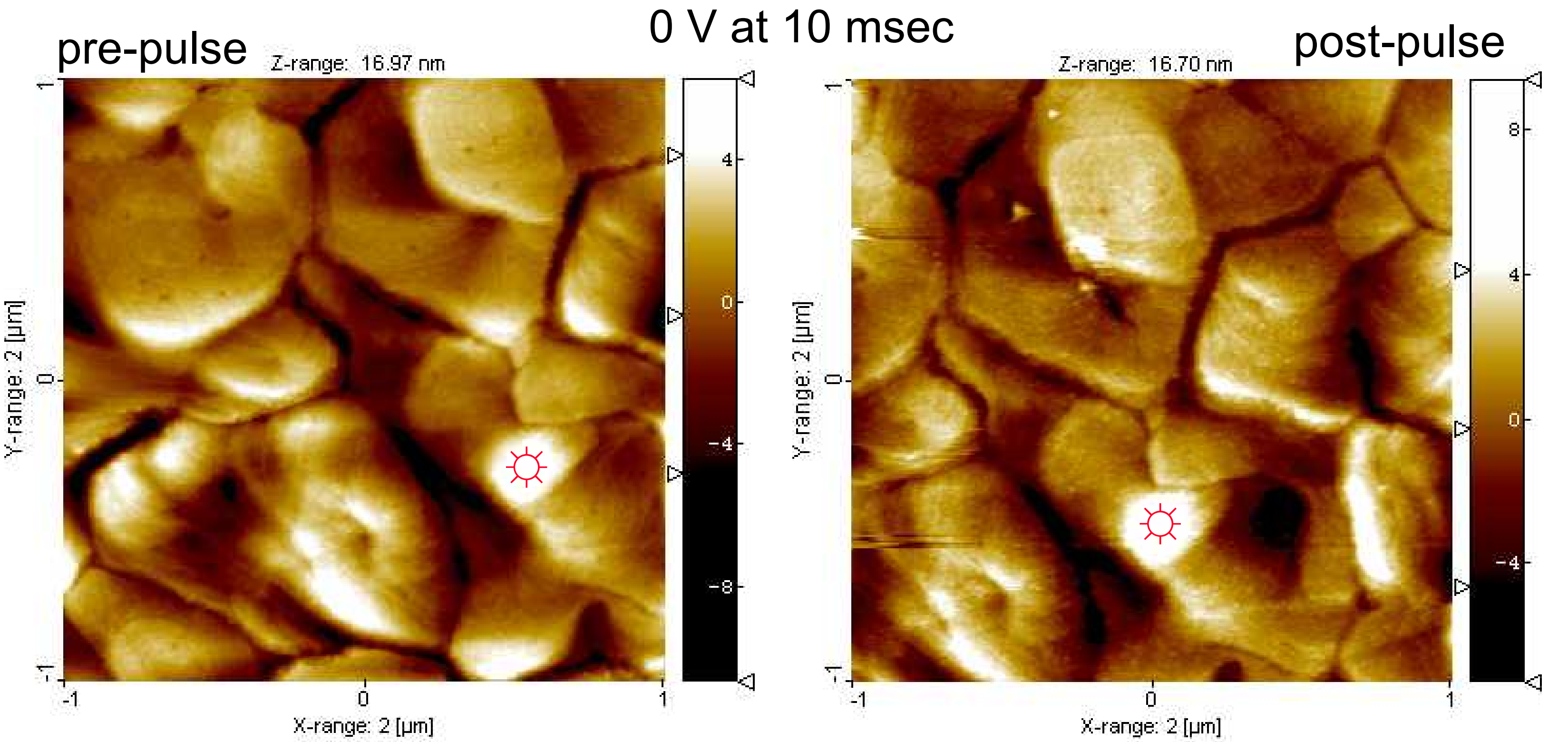
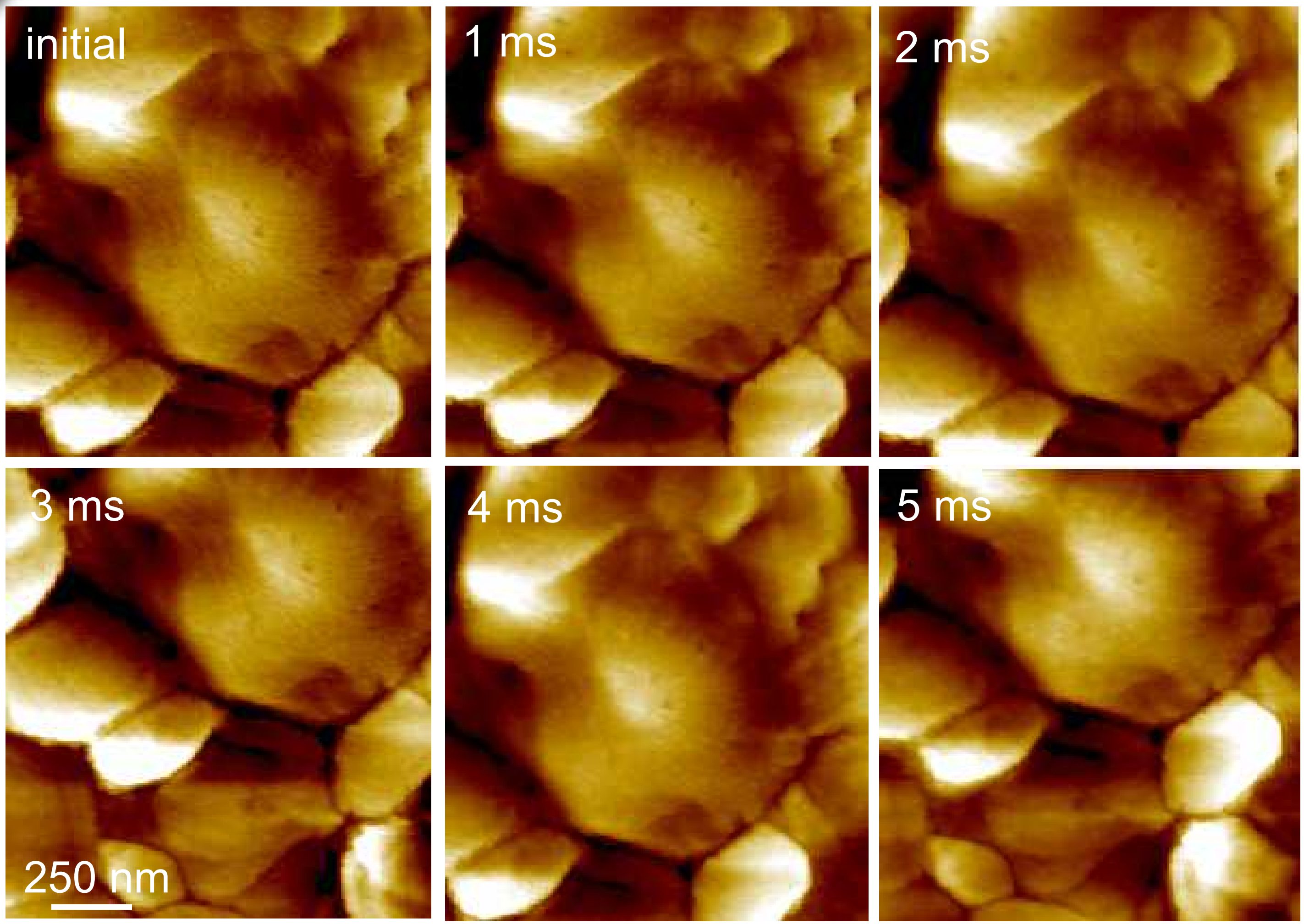
Low applied cell potentials at short times do not produce discernable impacts



tip instabilities demonstrate the difficulty of keeping tip-surface interaction attractive

Oxide platelet morphology is altered with repeated and longer potential pulses



1 V tip – sample potential pulse

transition from aligned platelet along growth steps to a more nodular structure - induced oxide growth

a specific degree of monitoring local site evolution appears possible

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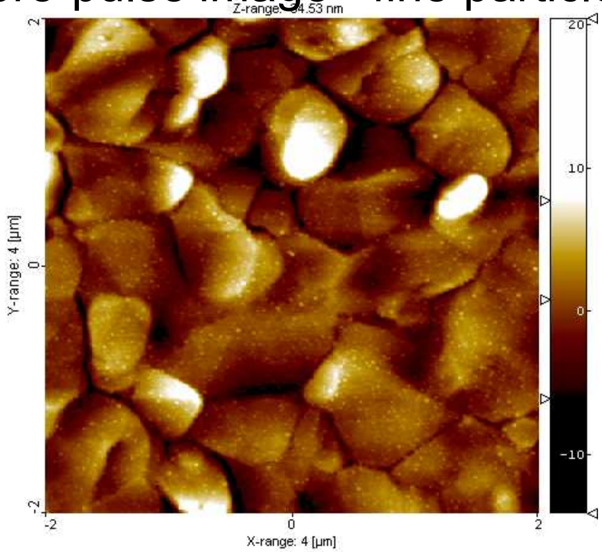
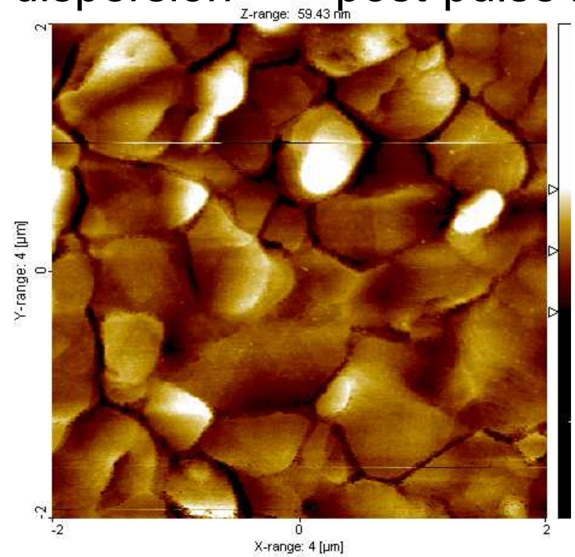
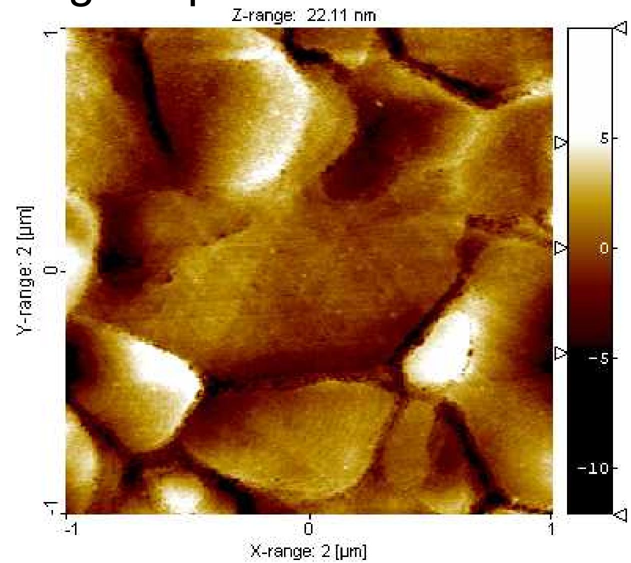
Response to a 1V, 1 sec potential pulse

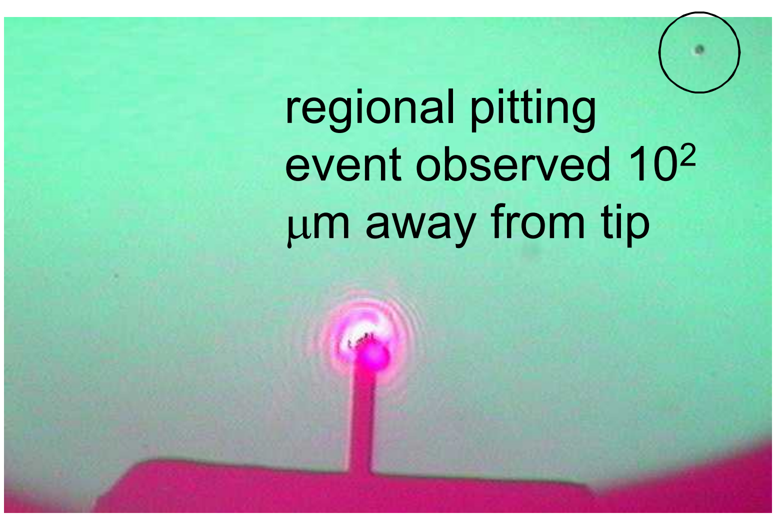
pre-pulse image - fine particle dispersion

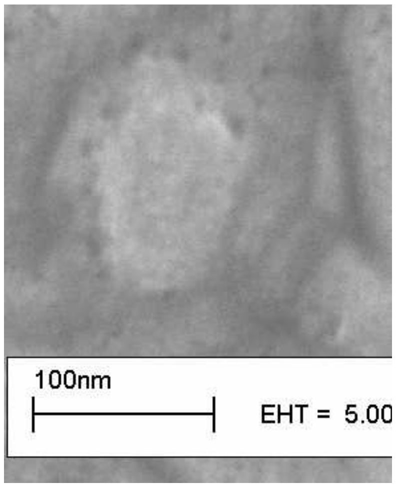


post-pulse images - particle loss









a fine pore structure appears at facet boundaries and edges

similar response to high rate current steps

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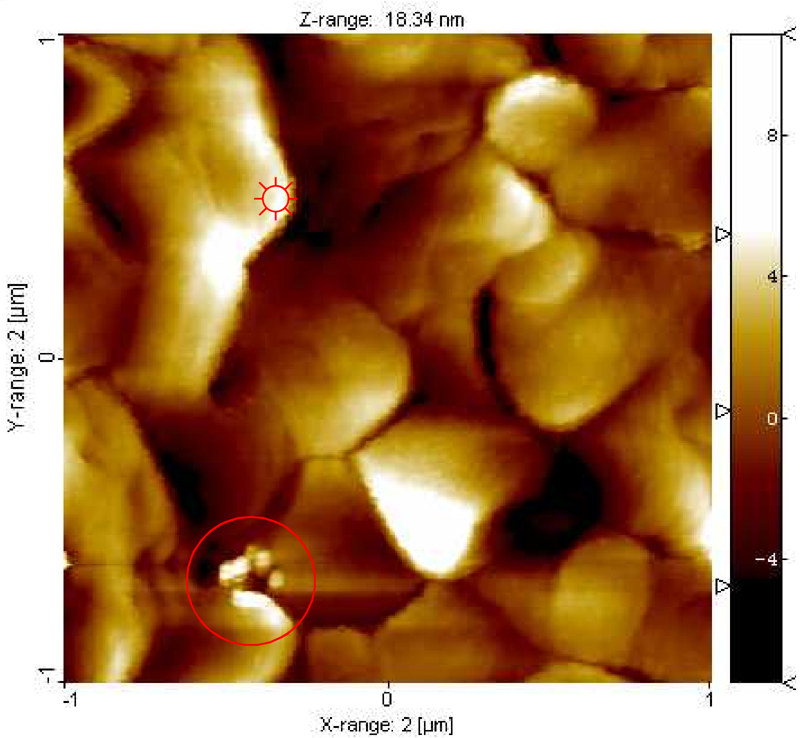
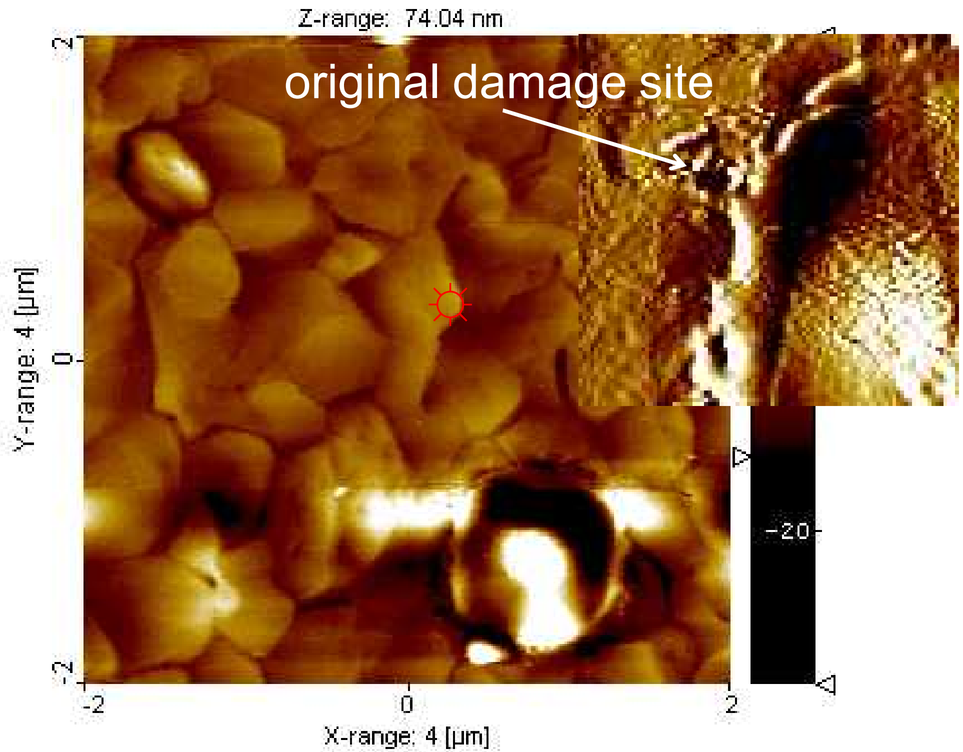
Unintended tip-surface interactions create undesired effects





Excessive lever amplitude damping observed during a slow tip retraction from the surface –repulsive tip contact

Post 0 V, 1 msec pulse apparently drove the resulting pit

Conclusions

- *in situ* high fidelity imaging of the mechanically complaint passive oxide on aluminum is possible

  operating in attractive mode AM-AFM is critical

- Localized anodic modification of the passive oxide is possible to monitor with *in situ* imaging

  anodic dissolution confined to the lever region

  nanopore formation at longer pulse times

- Current focus is to move toward higher frequency

  currently capable of 14 nsec pulses

  progressive sensitization of the oxide by potentiodynamic methods or repetitive pulsing

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