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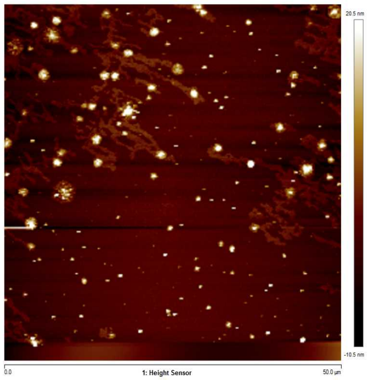

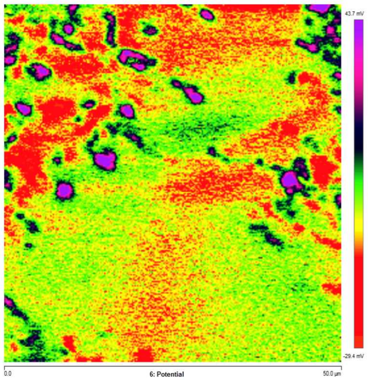

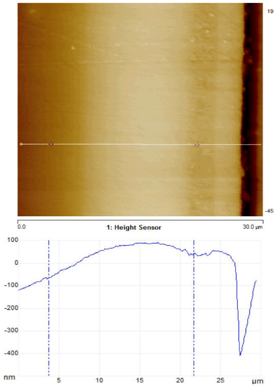

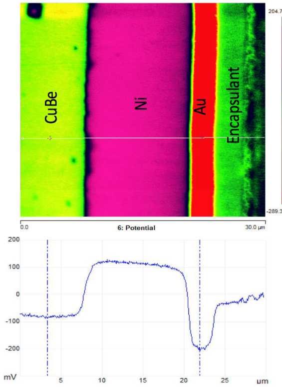

KPFM-AM as a *Potential* Tool for Probing Aging Evidence in Materials

Ana Baca, Michael Brumbach

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Motivation

- AFM electrical mode technique Development
  - KPFM
- Aging and/or degradation of materials is an important field tied to the reliability of materials in the future as well as harsh environments - corrosion, oxidation, diffusion

Aging on the Nanoscale
Current Research

PNAS

In situ nano- to microscopic imaging and growth mechanism of electrochemical dissolution (e.g., corrosion) of a confined metal surface

C. Merola[a], H.-W. Cheng[a], K. Schwenzfeier[a], K. Kristiansen[b], Y.-J. Chen[a], H. A. Dobbs[b], J. N. Israelachvili[b,1], and M. Valtiner[a]

[a]Department for Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH, D-40237 Düsseldorf, Germany; and [b]Department of Chemical Engineering, University of California, Santa Barbara, CA 93106

"One of the most important aspects of our finding is the significance of the electric potential difference between the film of interest and the opposing surface in initiating corrosion... When the electric potential difference reaches a certain critical value, the more likely corrosion will begin and the quicker it will spread. In this case, the nickel film experienced corrosion while the more chemically inert mica remained whole."

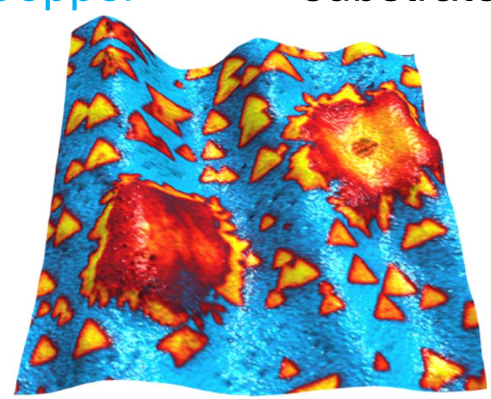
http://www.futurity.org/metals-corrosion-nanotechnology-1549742-2/

AFM-KPFM Applications

- The map of the **surface potential** produced by KPFM gives information about the composition and electronic state of the local structures on the surface of a solid observed at atomic or molecular scales along with topographical information.

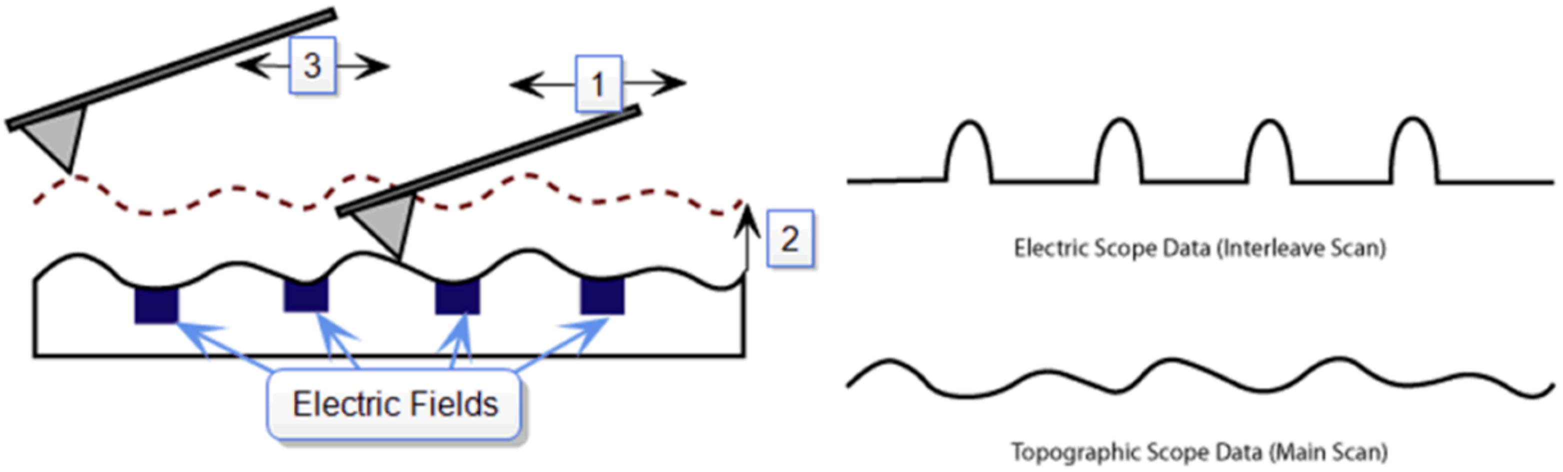
- The potential reveals surface phenomena including
  - Corrosion
  - Oxide formation
  - Doping of semiconductors/ microelectronics
  - Characterization of material blends/composites

Graphene – large lumps
Boron nitride – triangles
Copper - substrate



https://www.asylumresearch.com/Gallery/Materials/Surface-EFM/Surface11.shtml

KPFM Measurement



- To remove topography as a variable an interleave technique wherein
  - First pass tip detects topography
  - Second pass tip lifts to specified height and follows stored surface topography above sample
- Tip response is electrical influences - potential image

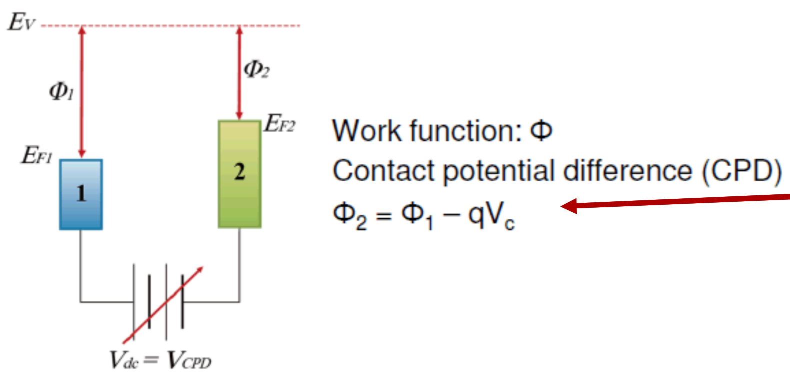
(Hua, Y. 2016 Advanced AFM Applications Training Class_KPFM [PDF document].Retrieved from onsite training, Bruker

Contact Potential Difference

- Electrostatic potential that exists between two electrically conductive materials (dissimilar i.e. with different work functions) that have been brought together in close proximity
  - Think parallel plate capacitor
- Work function- energy required to remove an electron from a solid to vacuum immediately outside the surface
  - *Can we use information about WF/CPD to determine if a material will still perform at its intended capacity???*

Images about work function, capacitors, etc.

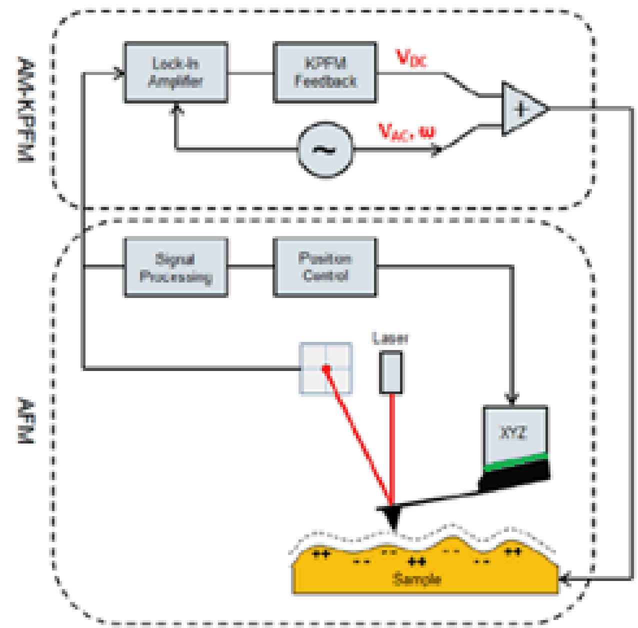
Φ = the energy it takes to remove an electron from the surface



CPD with calibrated probe yields sample Φ

How the Measurement is Taken

- Uses a conductive probe to image *work function* differences between the tip and the sample
- AC and DC bias is applied to the probe
  - AC bias is applied to probe’s fundamental resonance frequency
  - DC bias is adjusted through a feedback loop



This null condition occurs when the DC bias exactly offsets the work function difference

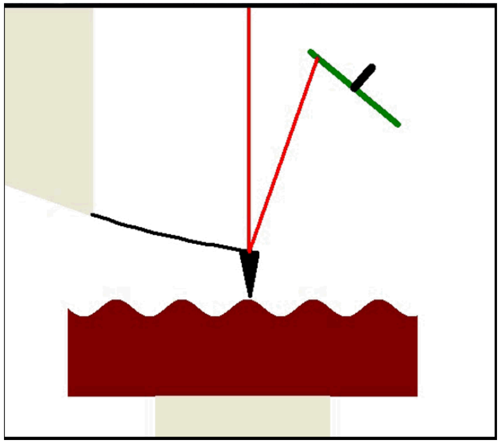
Quantitative Vs. Qualitative

- Quantitative measurements using AM-KPFM is difficult
  - Lower special resolution – stray capacitance
  - Surface cleanliness
  - Sample purity
  - Film thickness
  - Environmental conditions

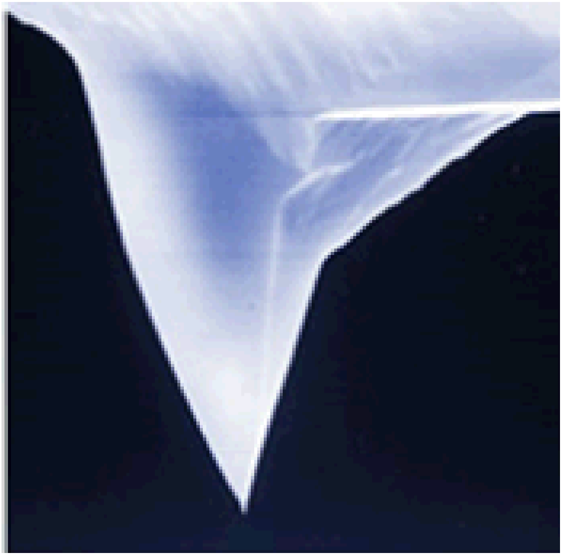
- Qualitative measurement
  - Correlate contrast in potential image
  - Topography
  - Can we correlate changes in potential as sample ages?

Mitigating Stray Capacitance

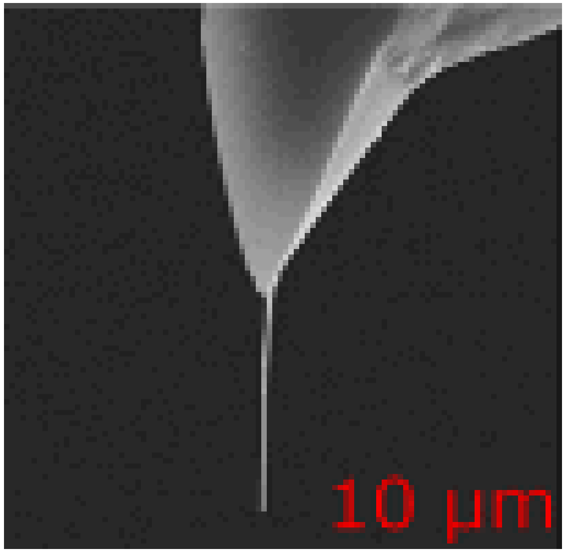
- Capacitance between cantilever and sample
- Needle tip to increase distance between cantilever and sample by ~10µm



Typical Tip

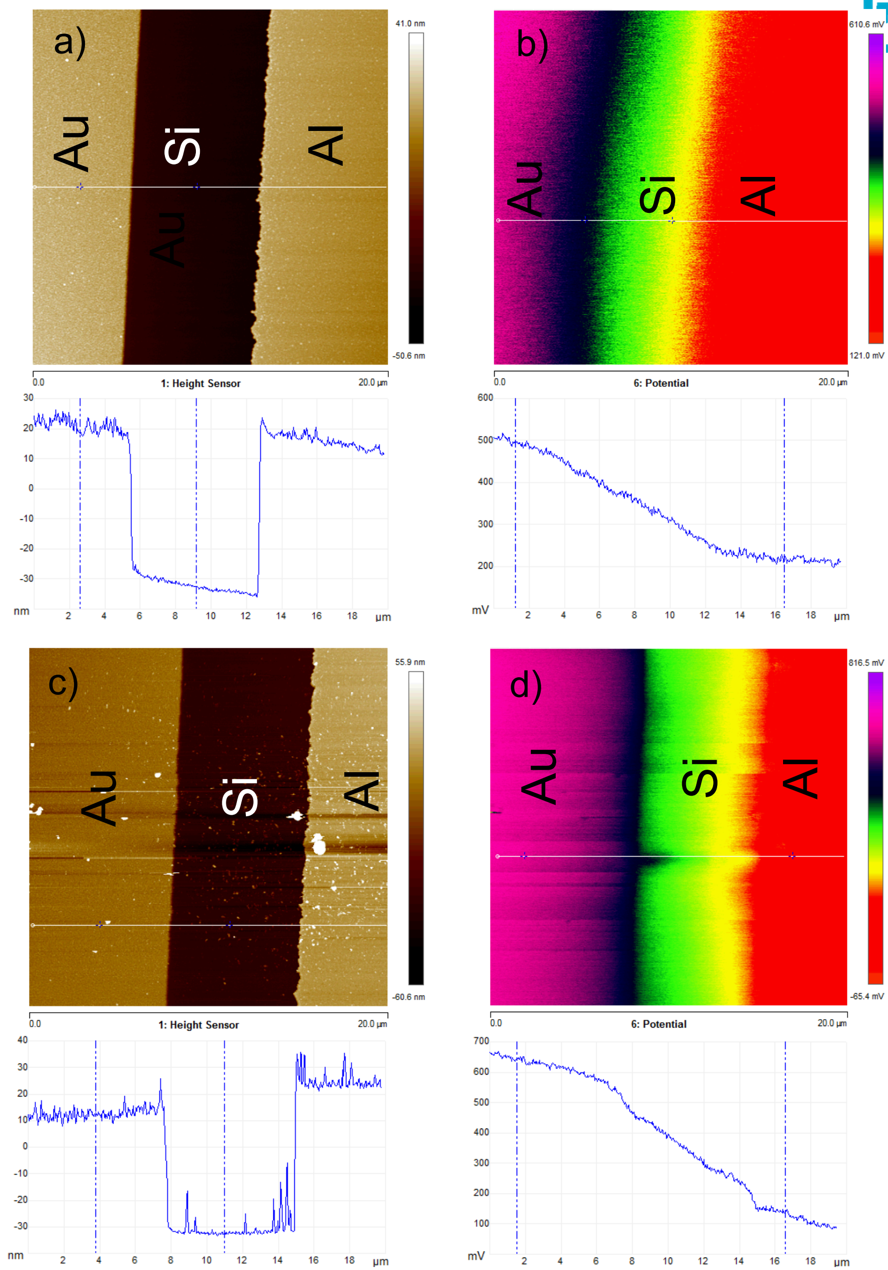


Needle Tip



KPFM Standard

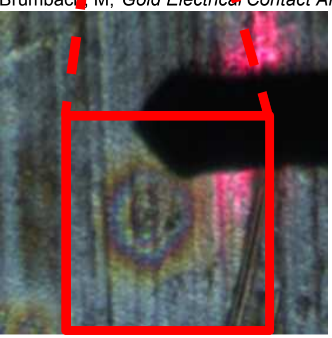
- Standard shows varying potential signal for relative material



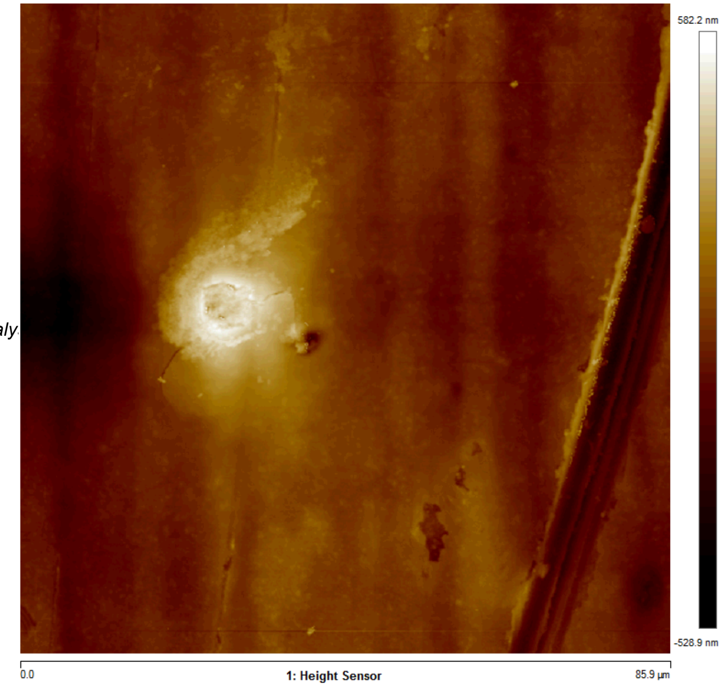
Au WF = 5.1-5.47ev
Si WF = 4.60-4.85ev
Al WF = 4.06-4.26ev

Gold ring (multilayered structure)

Brumbach M, *Gold Electrical Contact Analy*

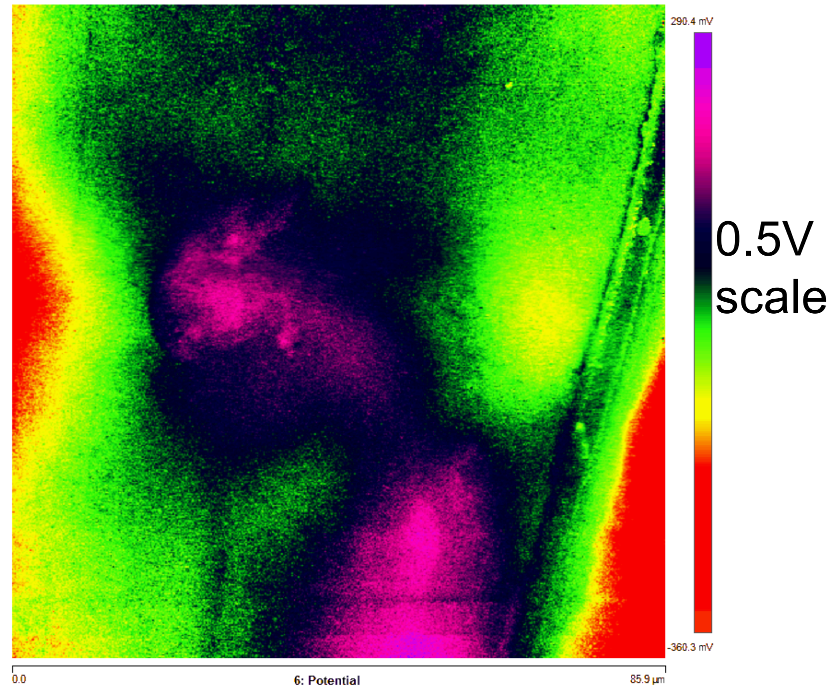


Height Image



90µm

Potential Image

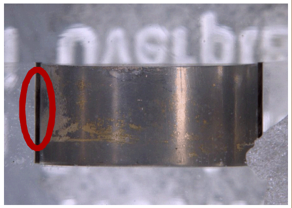


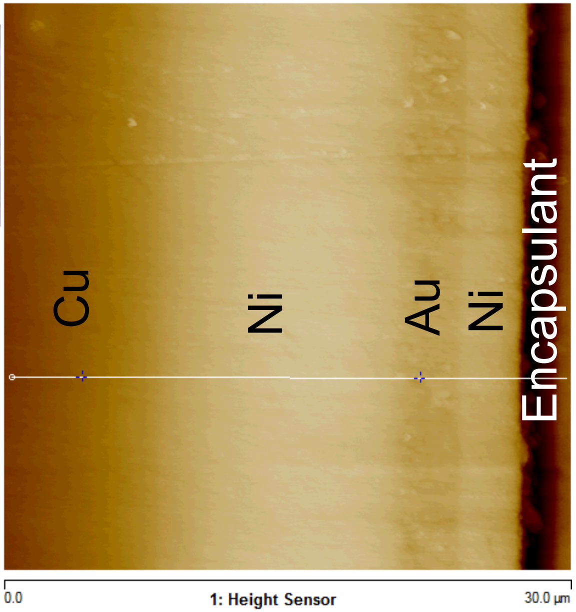
Au WF = 5.1-5.47ev
Cu WF = 4.53-5.10ev

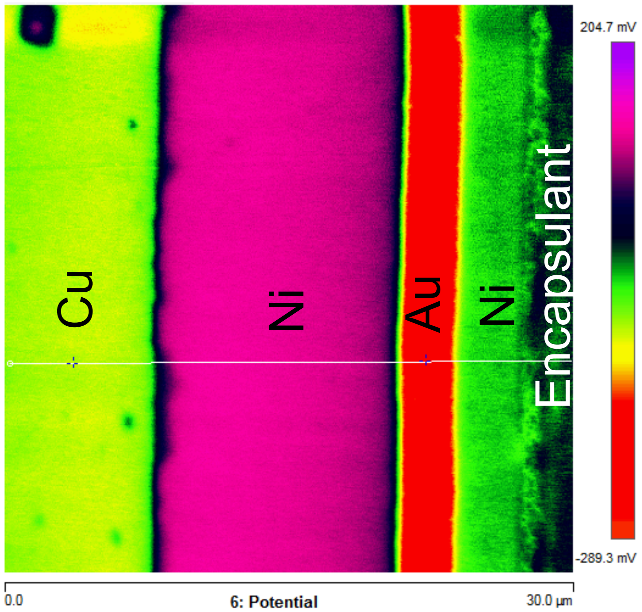
Visible evidence of chemical change

KPFM and potential image correlate to, but need more resolution

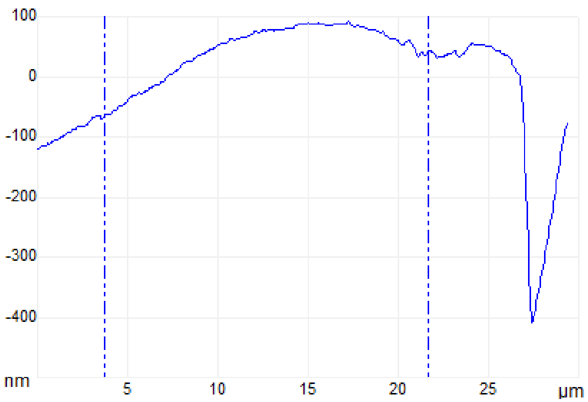
Cross-sectional Analysis

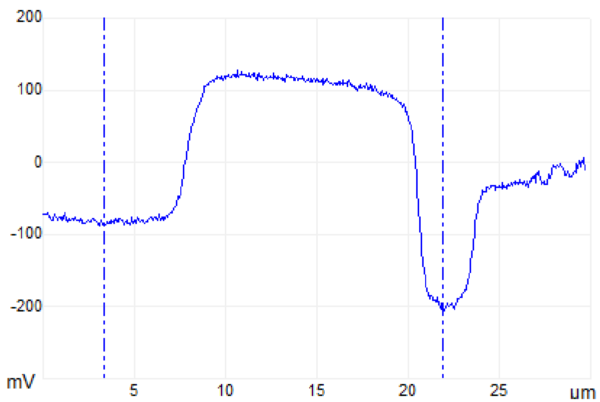






Sample was cross-sectioned, embedded in epoxy, and polished for analysis

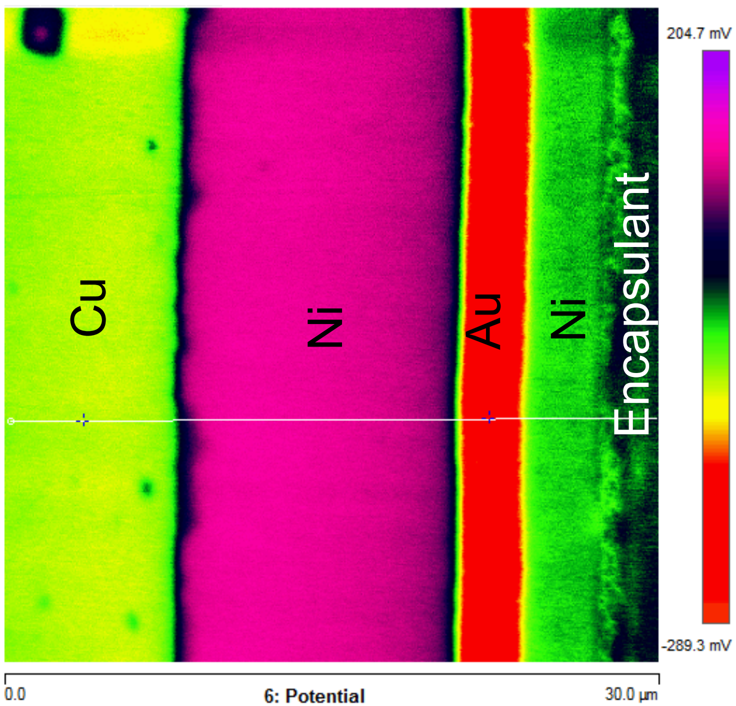


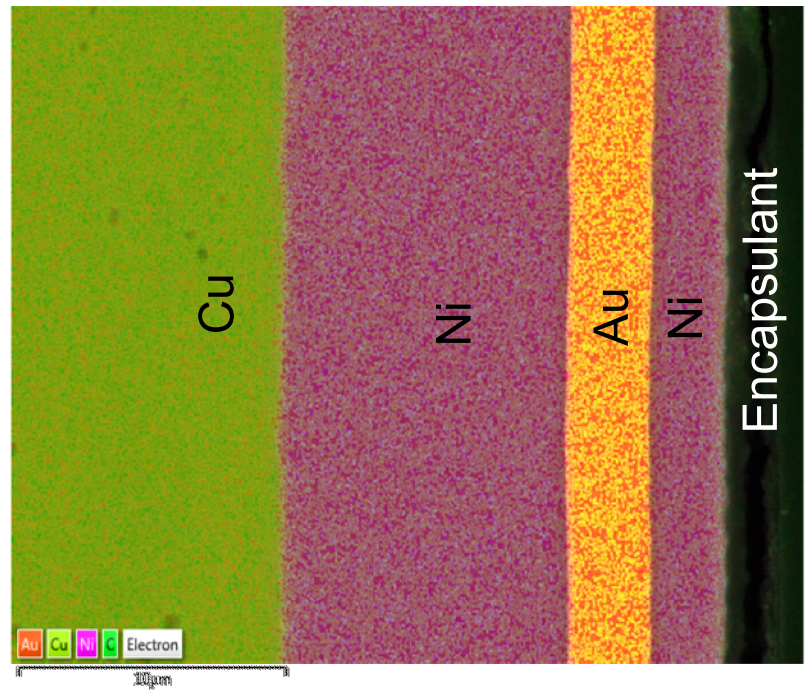


Topographically, fairly flat (bowing of sample due to polishing technique)

Cross Section Comparison to EDS

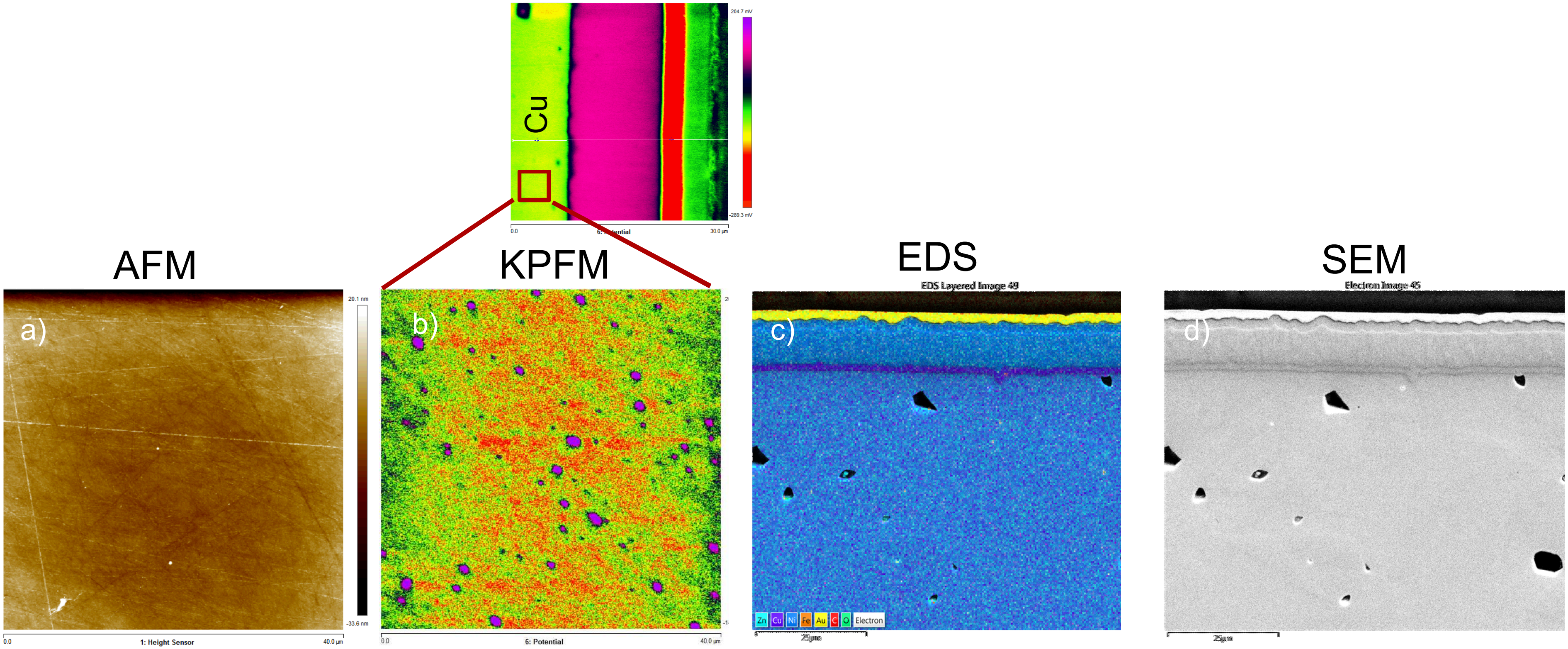
X-ray Dispersion Spectroscopy





- EDS reveals material composition
- EDS shows that the materials aren't diffusing into one another
- KPFM Interface effects are due to stray capacitance artifact

Center of Cross-Section

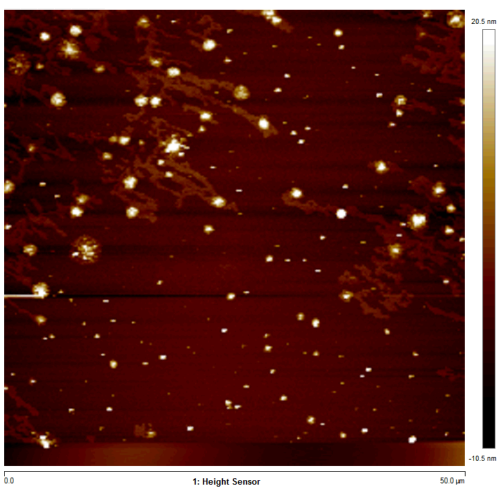


- Topographically smooth
- KPFM reveals potential contrast – not a topography artifact
- EDS reveals material composition – no material heterogeneity
- SEM – topographically smooth

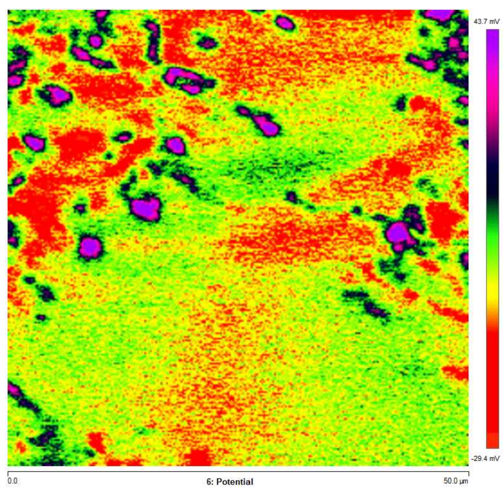
Thin Film - Subsurface Analysis

- Gold sputter deposition 16nm Au on Ti on Si wafer. Analysis after 6 years of aging
- Possible topography artifact
- Need addition analysis - Auger

AFM



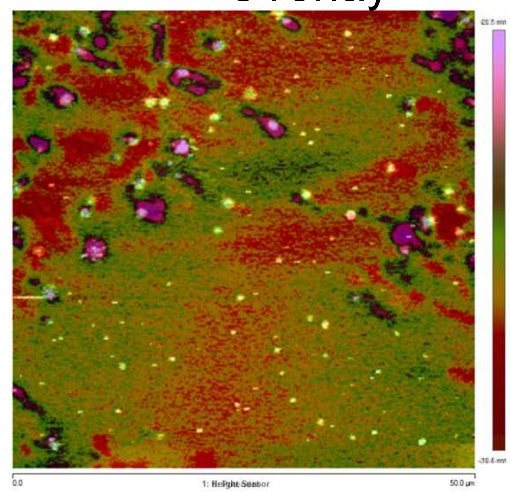
KPFM



Au WF = 5.1-5.47ev

Ti WF = 4.33ev

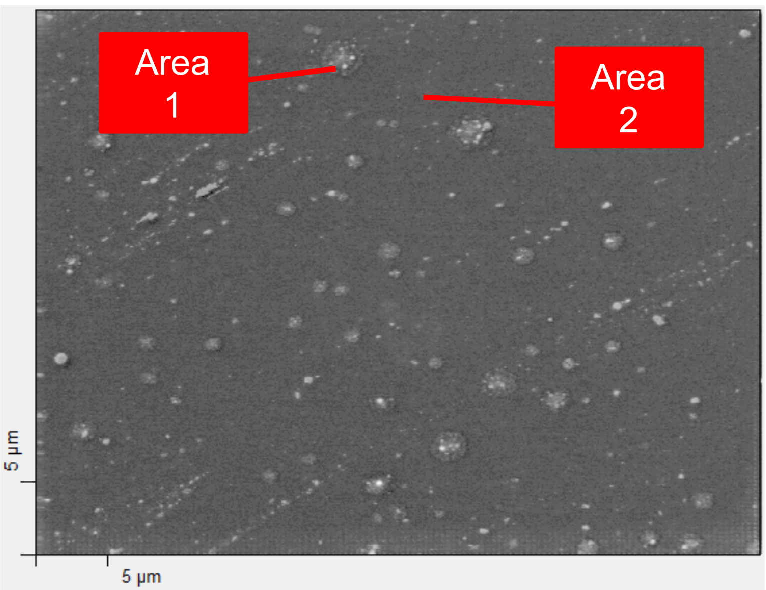
Overlay



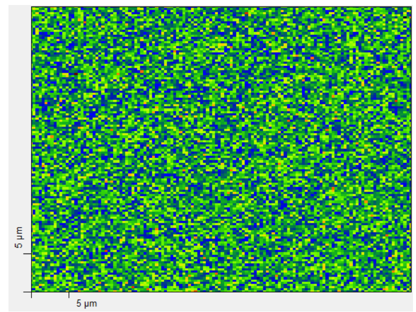
Auger Spectroscopy Analysis

- Top Au layer
- After 45s sputtering, analysis reveals Ti and O_2

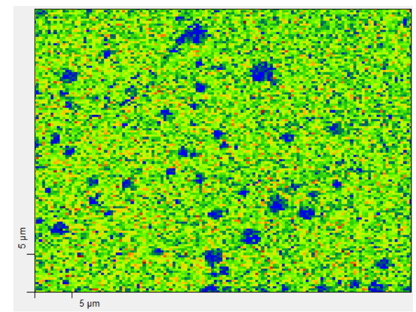
SEM



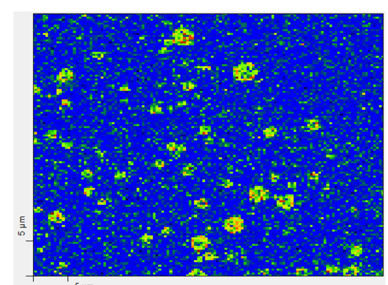
Atomic Concentration (%)			
	O	Ti	Au
Area 1	57.80	14.92	27.28
Area 2	7.22	59.75	33.03



Gold t=0s



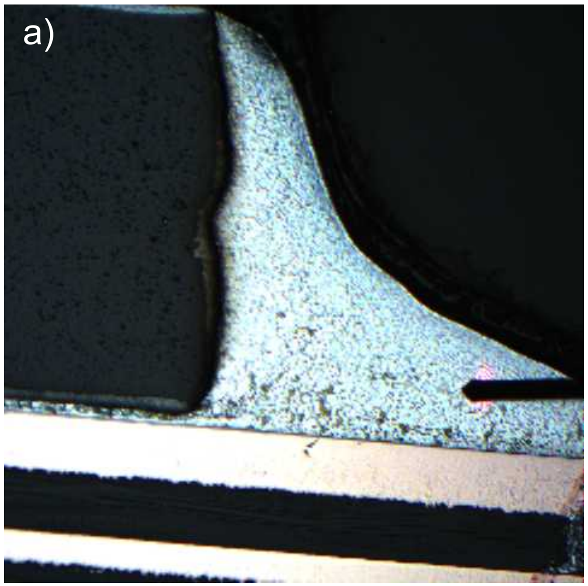
Titanium t=45s



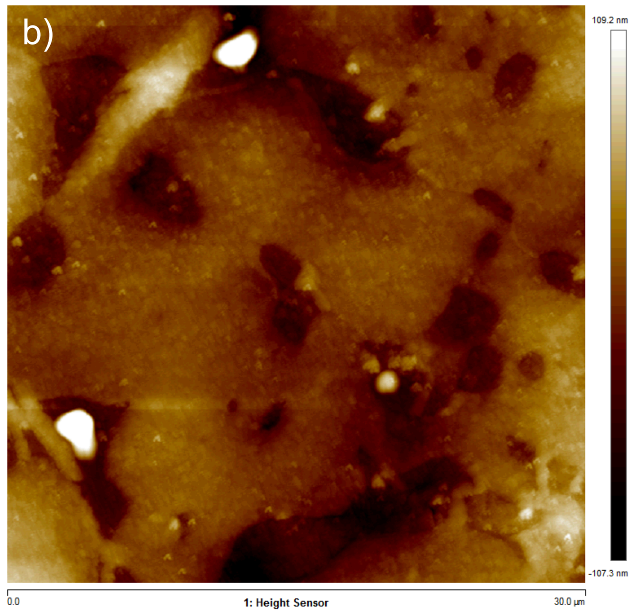
Oxygen t=45s

PbSn Solder Joints

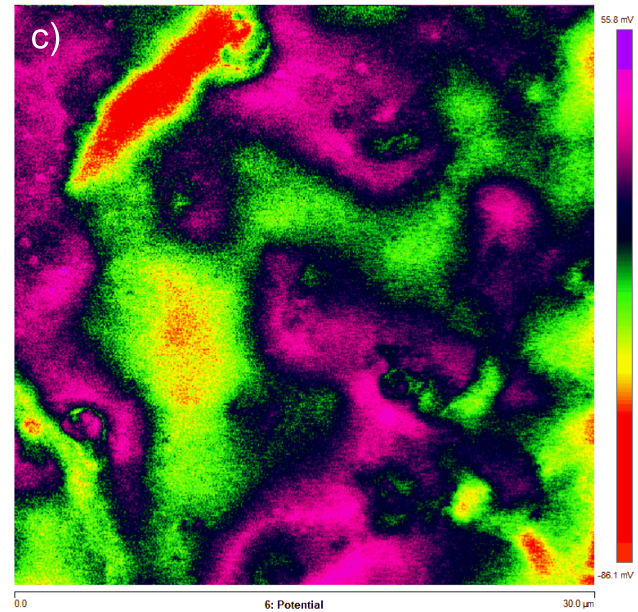
Optical



AFM



KPFM



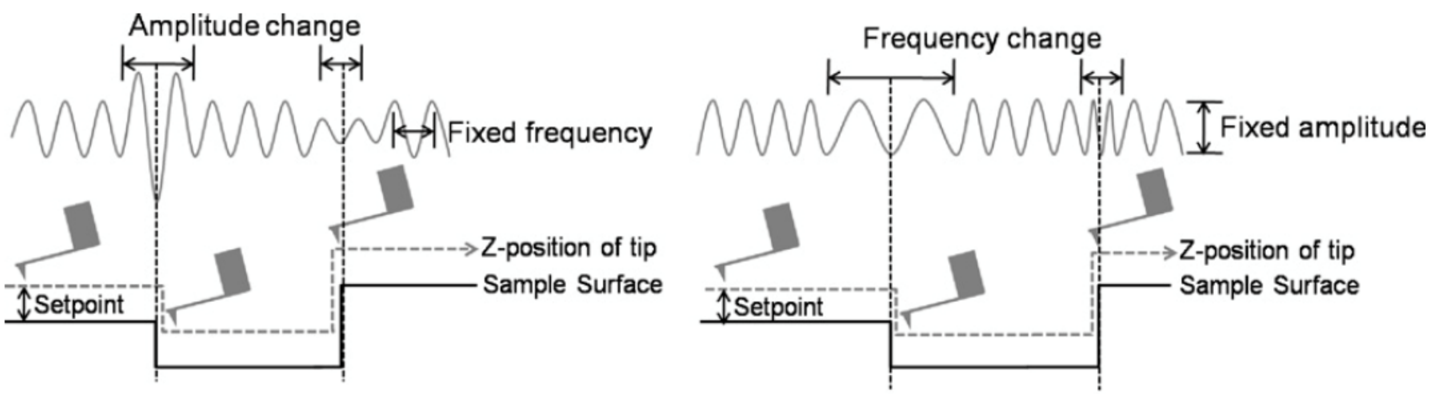
- Good candidate for aging studies
  - tin will coarsen as it “ages”
  - Coarsening coupled with potential contrast will reveal degree of aging

Conclusion

- We were able to validate and optimize the technique using current instrumentation available
- Investigated aged materials and saw differences/ evidence that changes were occurring at the surface
  - Were able to identify differences in chemical potential not evident by other means/instruments readily available (no visible indicators, etc.)
- An FM-module has been ordered- we look to reproduce these experiments with higher spatial resolution
  - Better define the extent of evidence of corrosion
  - Attempts at quantifying the CPD

AM- vs FM Mode

- Complex explanation using feedback modes
- Introduce difference between AM and FM modes



- AM has higher signal to noise ratio, FM more sensitive laterally
- We wanted to test the limits of our current AM module to see if there is potential use for this technique... and is it worth improving?