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ToF-SIMS Data Analysis - Methods and Challenges

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Wren, 0136, 16:00

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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Outline

- Introduction
  - SIMS Process / Sources of Contrast
  - Goal
- Multivariate analysis introduction and example
- Sample topography is the key
- Sample topography affects both 2D and 3D analyses
  - How does topography affect 2d analysis
  - Separating topographical contrast from chemical contrast
  - 2D examples
  - Methods of removing 3D distortion
  - 3D Example
- Methods of acquiring surface topography
- Future Work
- Conclusions

Time-of-Flight Secondary Ion Mass Spectrometry is a Complicated Technique

- SIMS is a technique governed by many competing processes.

Instrument
  - Primary ion species and energy
  - Extraction and analyzer performance
  - Detector response
  - Gross and local field effects

Sample
  - Matrix effects
  - Ionization effects
  - Surface charging
  - Magnetic domains
  - Concentration
  - Topographical effects

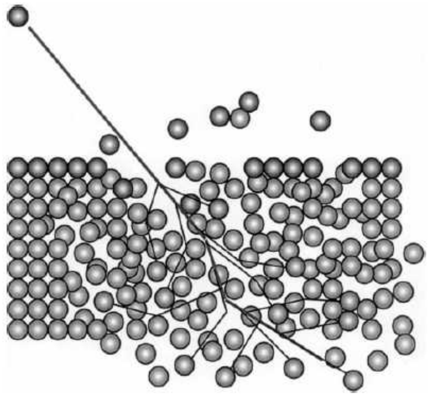

Fig. 1. Schematic representation of the sputter process (trajectories are given for primary recoil atoms)

Hagengoff, Mikrochim. Acta 132, 259-271 (2000)

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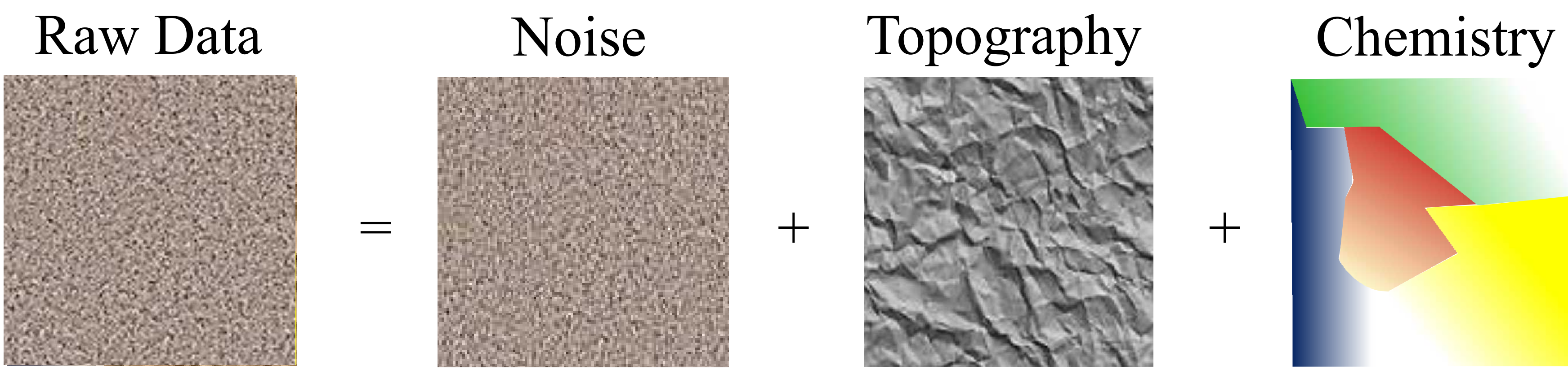
Goal

Extract the most information from the SIMS technique by isolating noise or other causes of contrast from the chemical information of interest.



Ultimate goal: Provide the highest fidelity SIMS data analysis in order to accurately determine chemical signatures, trends and feature sizes.

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Can Acquire Several Types of Data with ToF-SIMS

- Surface imaging
  - Most interested in fragmentation patterns of the undisturbed surface.
  - Chemical signatures can be very complex and contain overlapping peaks.
- Depth profiling
  - Because of damage during the profile, most organic fragmentation is lost and spectra are much less complex. (Historically. This is changing with some cluster sources.)
  - Monitor concentration versus depth.
- Imaged depth profiling (3D analysis)
  - 3-dimensional spatial information over a significant depth.
  - Usually monitor inorganic or highly fragmented organic signatures.

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Multivariate Analysis is a Powerful Tool for ToF-SIMS Data Analysis

- Multivariate analysis distills large and complex datasets into easy to understand and manage components.
- Has been applied to spectral series (1D), images (2D) and depth profiles (3D).
- Multivariate analysis factors data into components:

$$D = C_n * S_n^T$$

Where: D = SIMS spectral series

C = Concentration vector (scores)

S = Spectral Vector (loadings)

n = Component number

  – Many multivariate algorithms have been used:
    - PCA (Principal Components Analysis)
    - ALS (Alternating Least Squares)
    - MAF (Maximum Auto-correlation Factors)
    - Rotated PCA

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Multivariate Analysis (continued)

- The problem: All multivariate methods assume that data is linear with concentration.
- One must use the appropriate scaling in order to make concentration and noise linear.
  - If non-linear, extra components will be needed to describe the non-linearity of the data.
  - For ToF-SIMS, binomial model seems to be most appropriate as it accounts for detector dead time and for Poisson noise concurrently.
    - Keenan, Smentkowski, Ohlhausen, Kotula, Surf. Interface Anal. 2008; 40:97-106.

Multivariate analysis in and of itself knows nothing about the sample or the technique. It is only a mathematical procedure.

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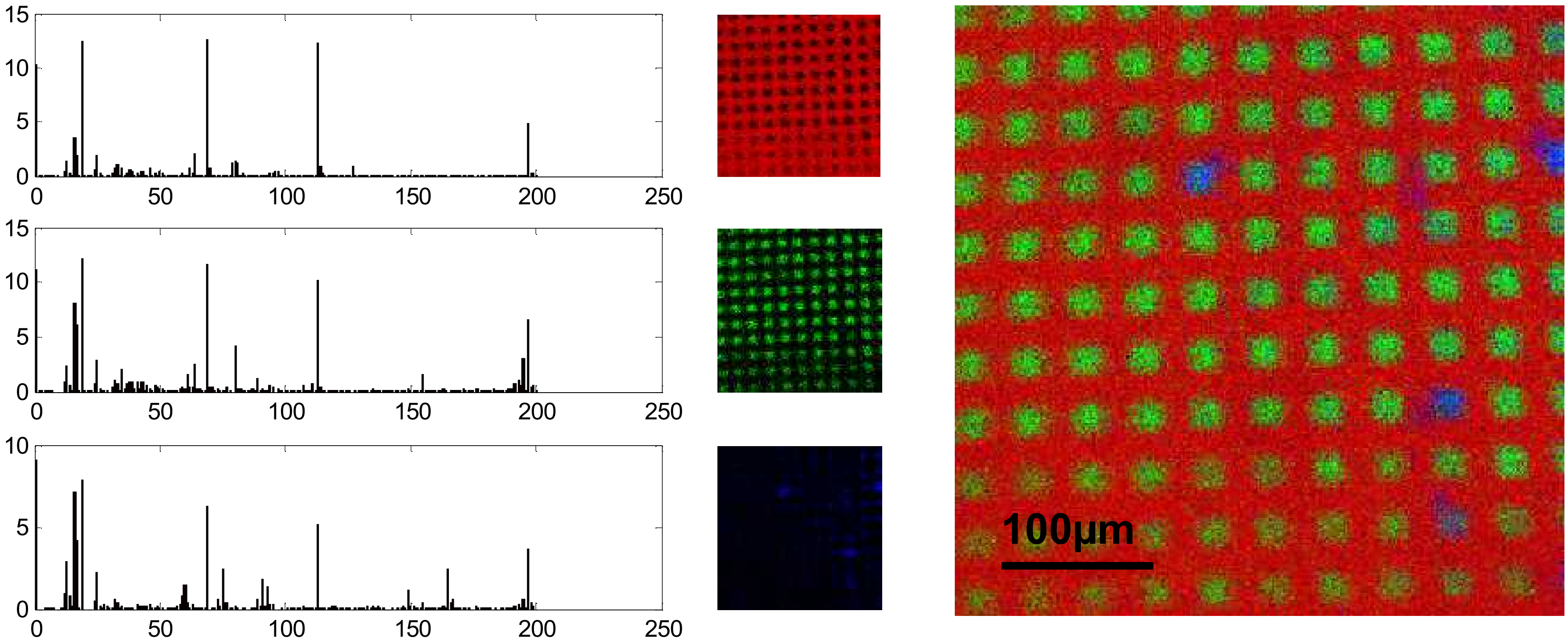
Multivariate Analysis Provides Detailed Chemical Phase Information



This simple ALS example demonstrates the ability of MVA to isolate the peaks that cause contrast in the image.

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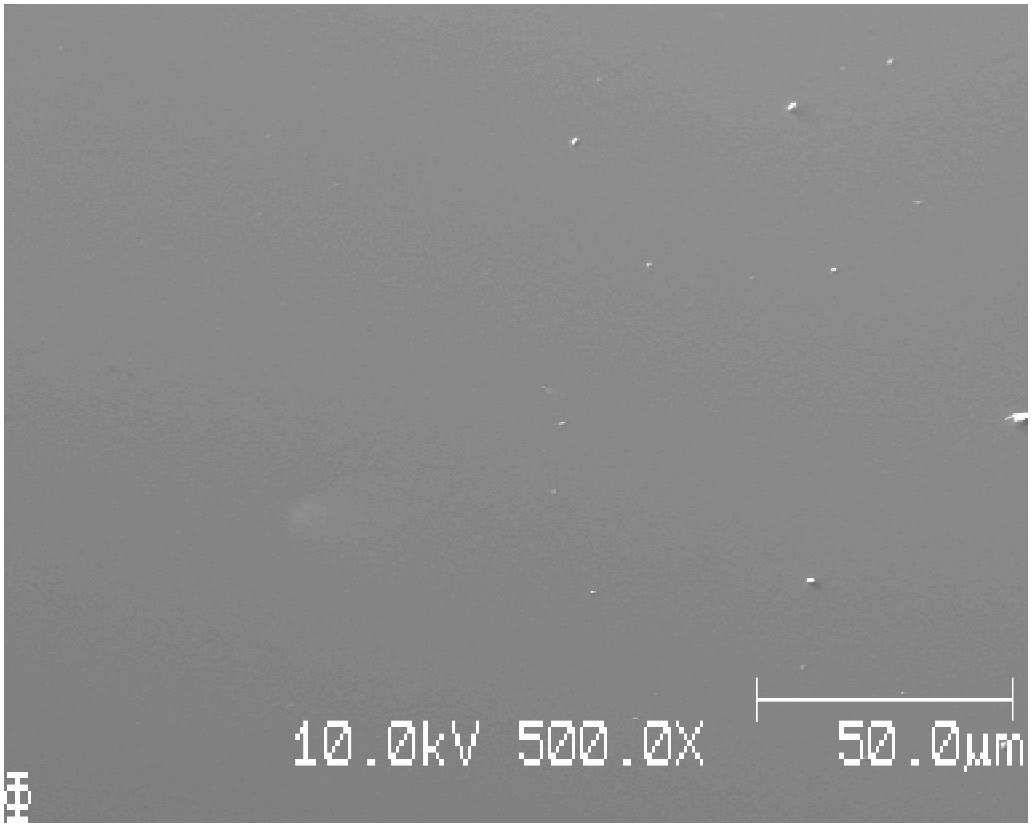
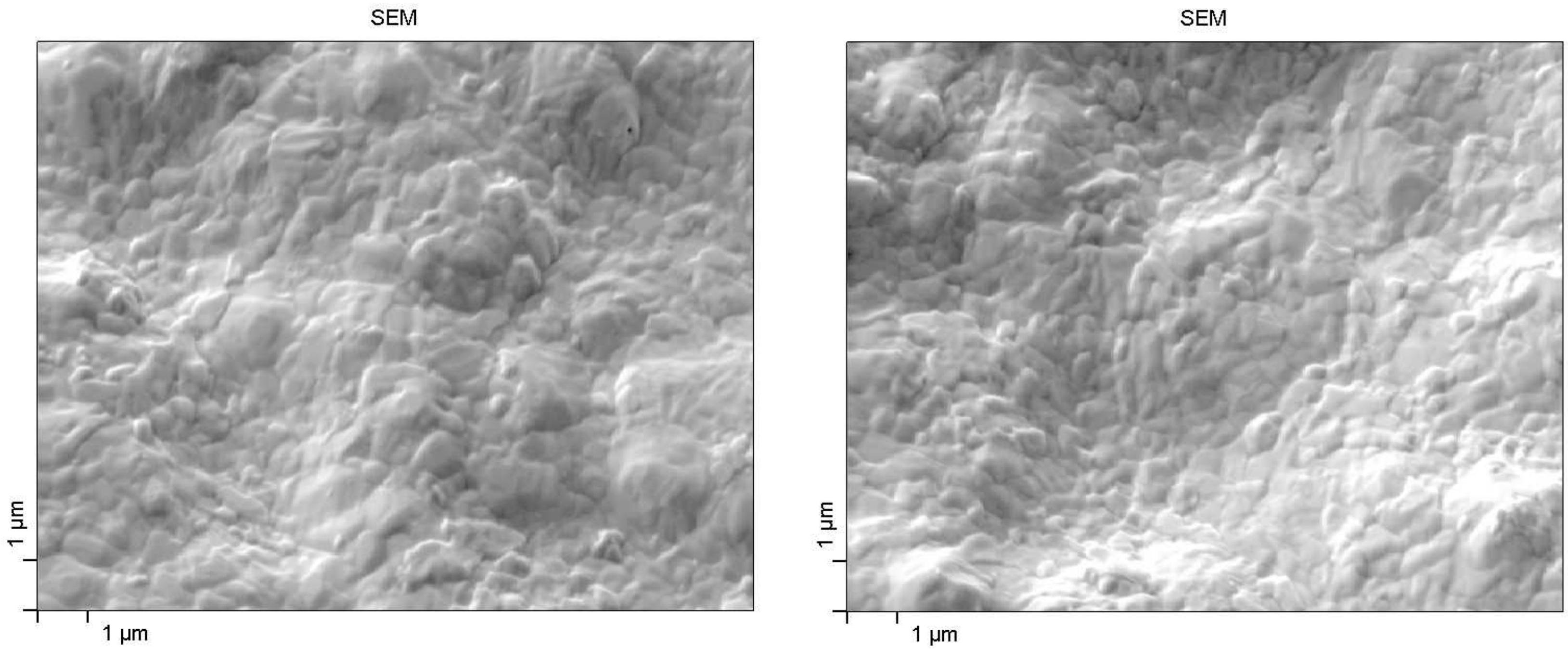
The Ideal Sample is Flat and Featureless



45-nm SiO_2 on Si substrate

In the industrial laboratory, we usually do not have the luxury of ideal samples.

Most Real Samples Have Topography



Processed Au Layer, 250^{0}C, 2 hrs, N_2

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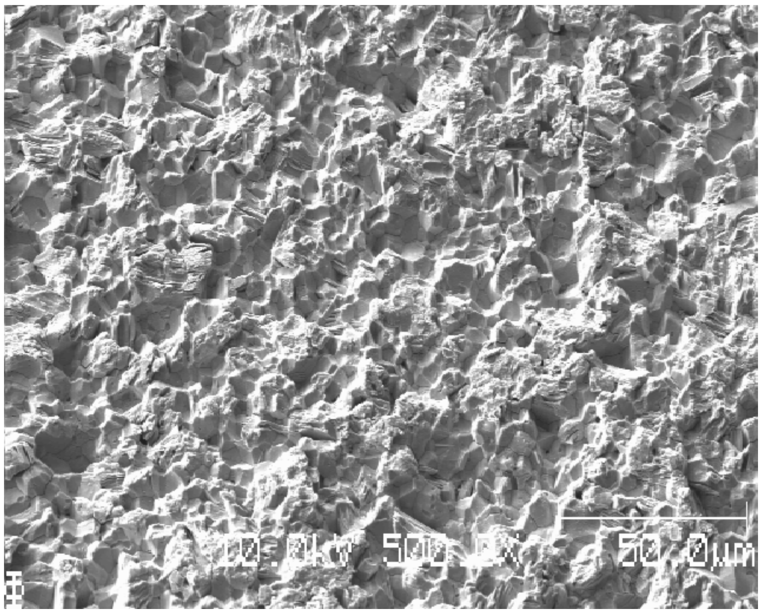
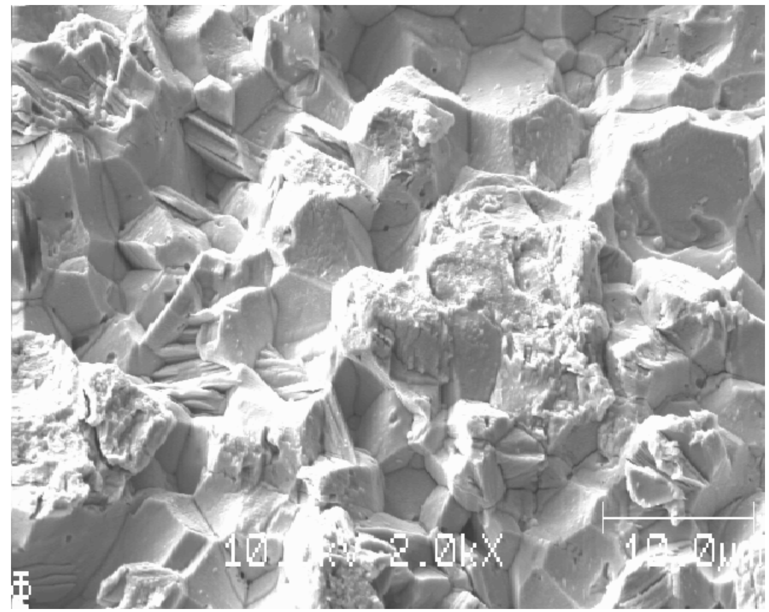
Some Samples are Extremely Rough





Metal alloy / 200-nm Ni / 200-nm Au layer

Many times topography is not understood at the time of analysis.

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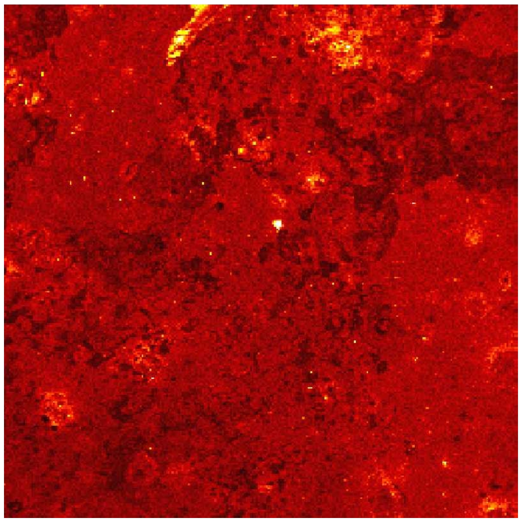
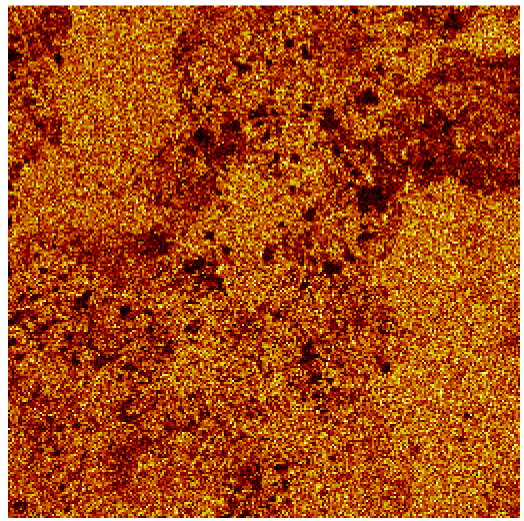
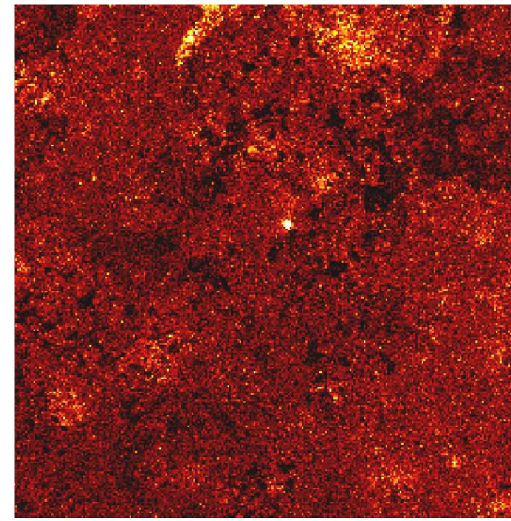
Without Measuring Topography, It's Influence is Unknown



Total Ion Image



Si^+



CF_3^+

Is the contrast in these images chemical or topographical related?

Topography Can Cause Significant Spatial and Yield-related Distortions

- 2D Images
  - Disturbs even field lines, changing the path of the extracted ions.
  - Sputter yield varies with surface angle
  - Topography causes spatial distortions
- 3D Volumes (Just a series of 2D images!)
  - All of the above plus…
  - Topography causes distortions in rendered 3D volumes.
  - 3D volumes also distorted by sputter angles.

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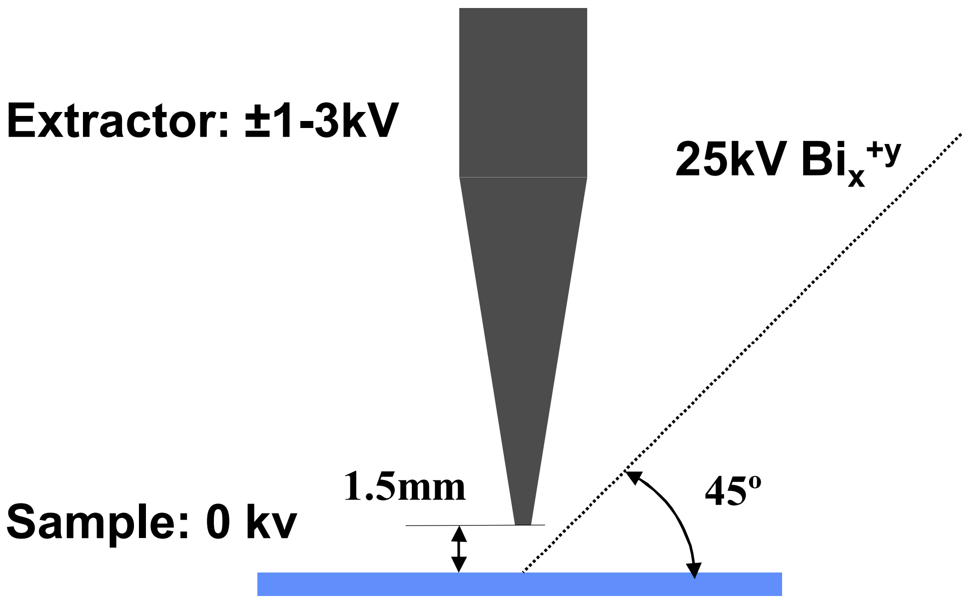
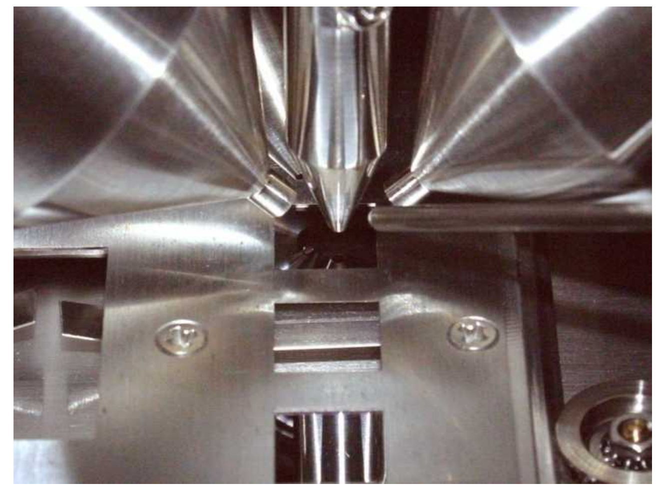
Topography Causes Non-chemical Distortions and Contrast

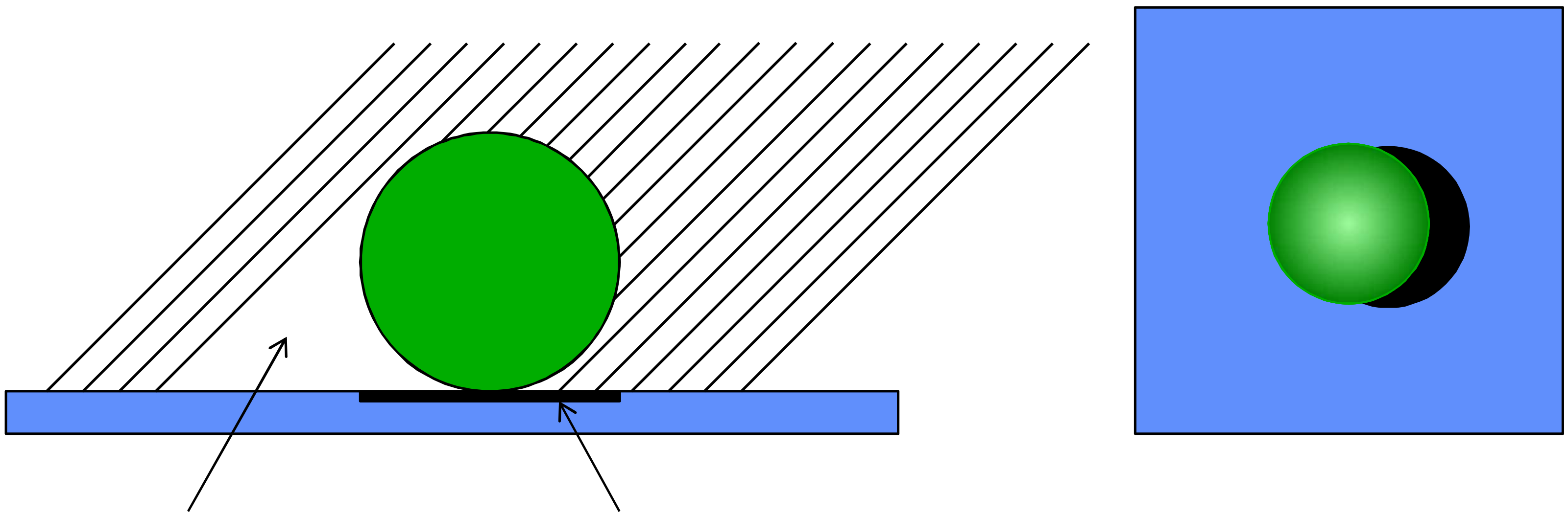




When interpreting images, must account for topography:

- Spatial distortion due to perspective
- Angle-related sputter yield

When Imaging a Sphere, Expect to See:



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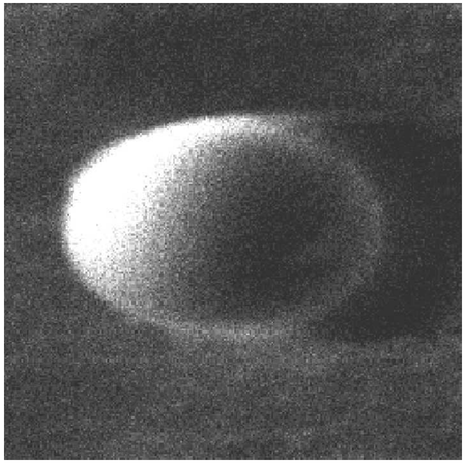
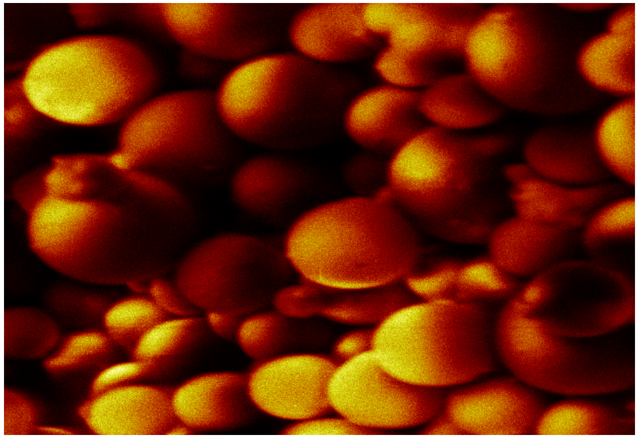
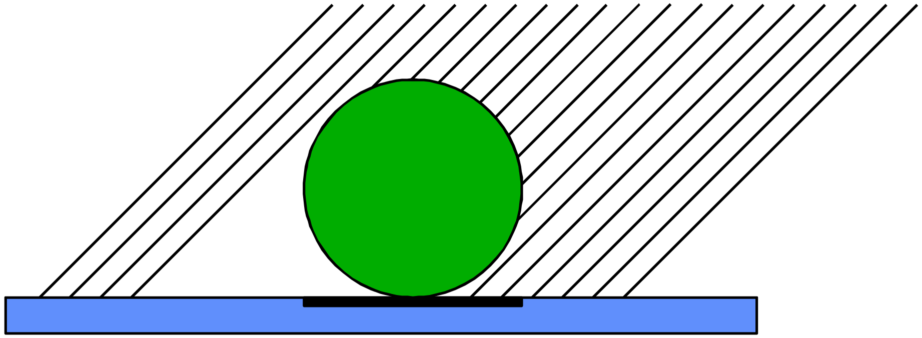
But, we actually see

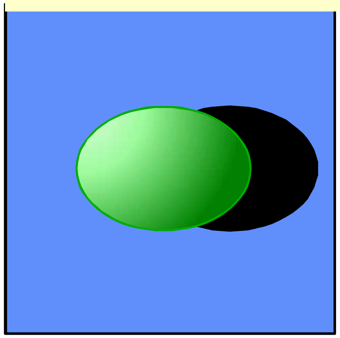


Sphere is elongated in the x direction.



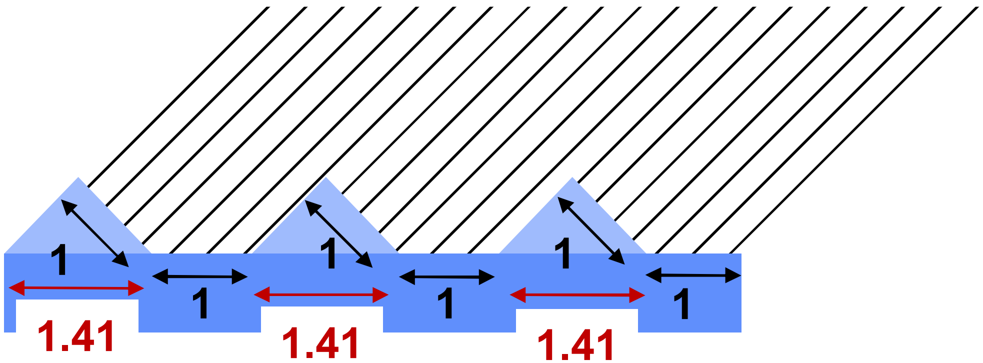
Effect is reproducible

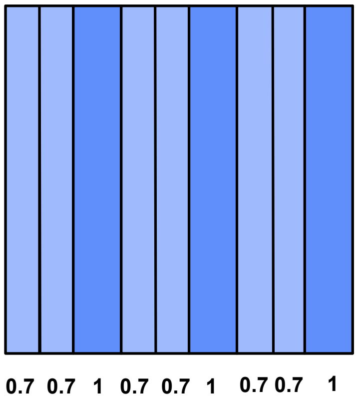




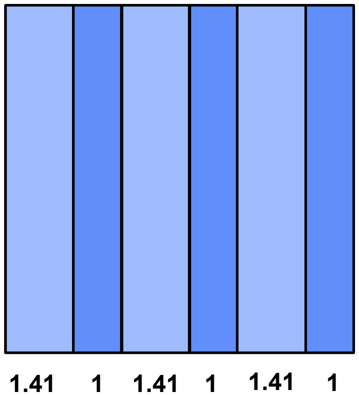
What causes this unexpected distortion?

Spatial Calibration Assumes a Flat Surface

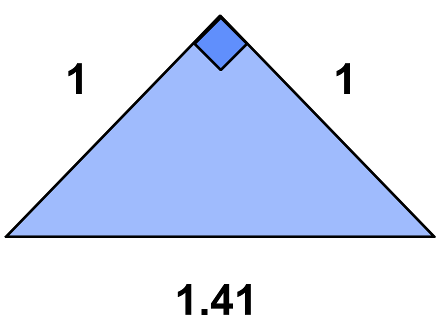




Top View



SIMS View

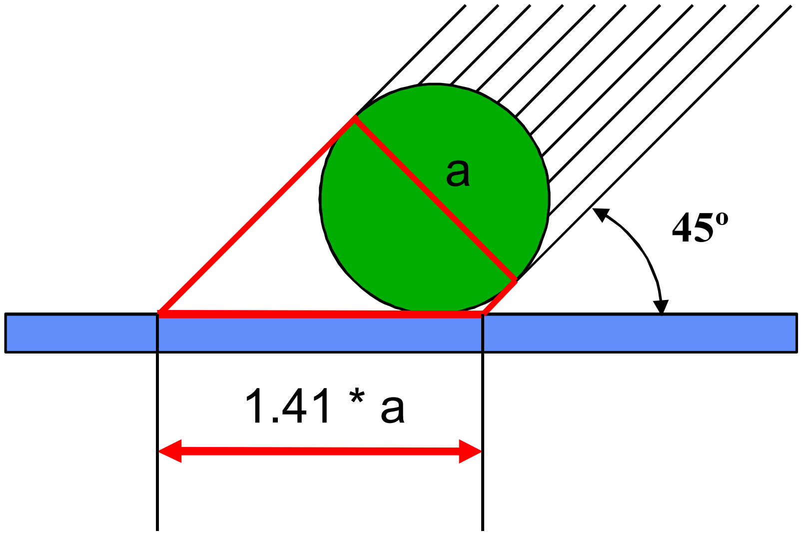


$$\sqrt{1^2 + 1^2} \equiv \sqrt{2} \equiv 1.41$$

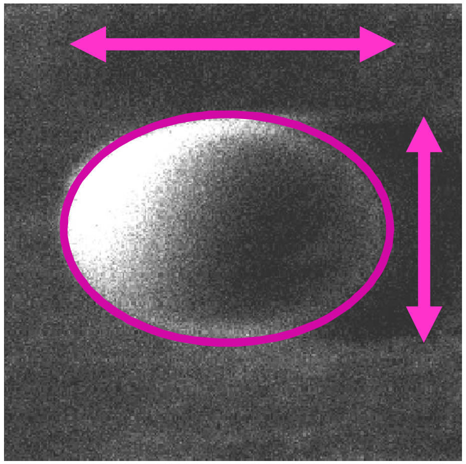
- **Distorted Image**
- **Totally miss back side of structure.**

Perspective-related Spatial Distortion is Predictable

A sphere appears as a 45 degree object with curvature.



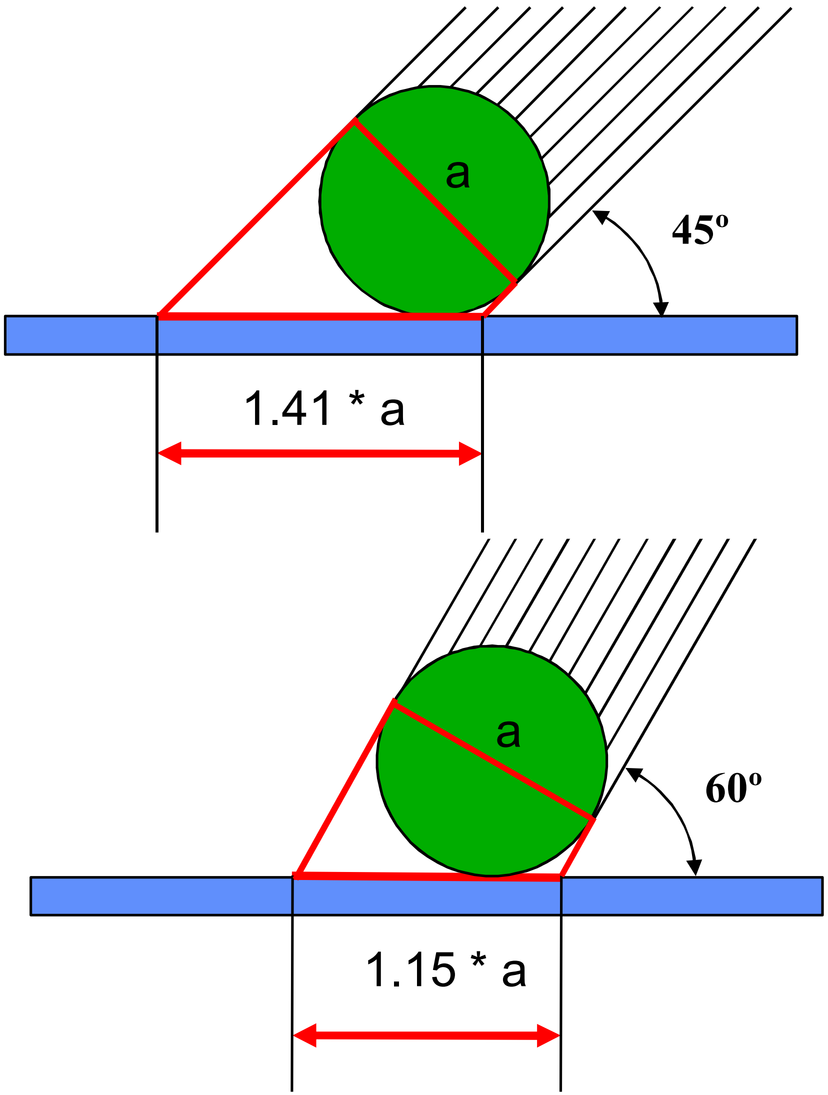
1.41



1

Aspect ratio is exactly 1.41:1!

Other Instrument Geometries Yield Different Distortions



ION-TOF **PHI TRIFT**

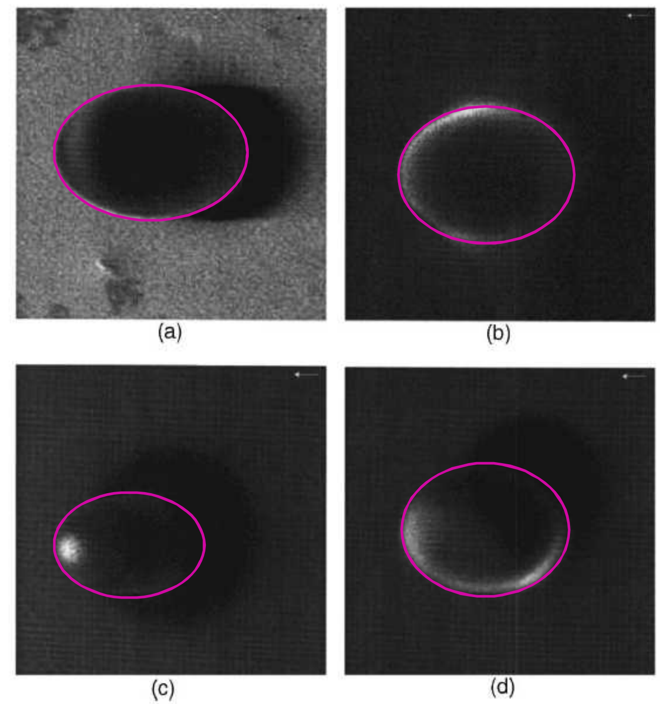
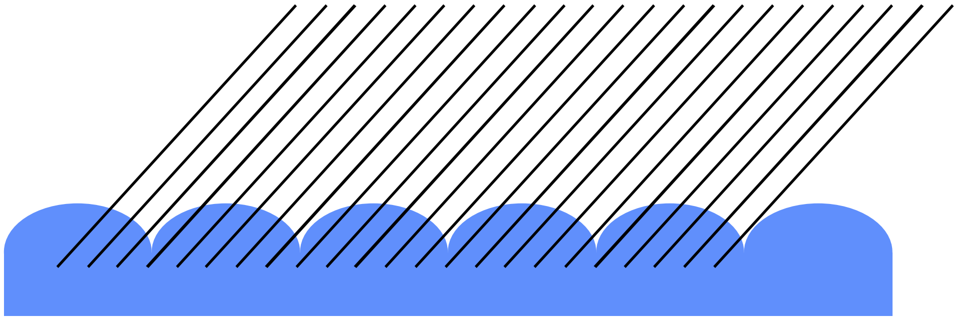
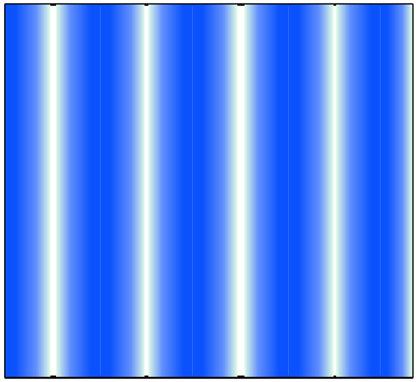


FIG. 5. 80 × 80 μm^2 total ion images of microspheres: (a) Pluronic coated PS sphere on a glass substrate using a reflectron instrument, (b) Pluronic coated PS sphere on a silicon substrate using a TRIFT instrument, (c) gold coated sphere using a reflectron instrument, and (d) gold coated sphere using a TRIFT instrument.

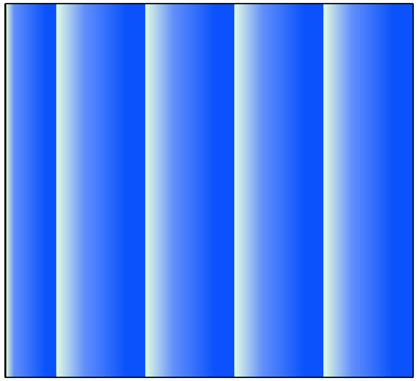
Rangarajan & Tyler, J. Vac. Sci. Technol. A 24(5) Sep/Oct 2006

It’s a Matter of Perspective



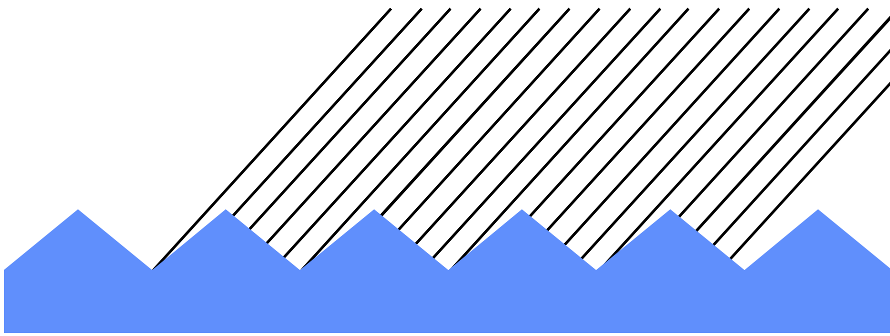


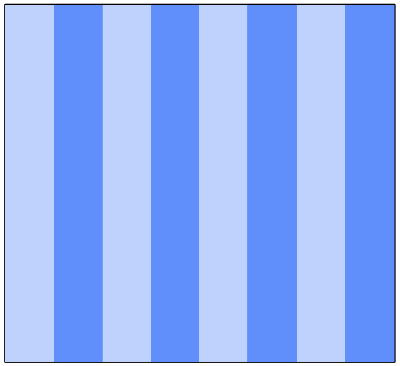
Top View



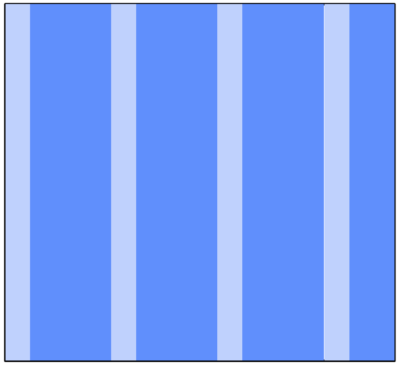
SIMS View

It’s a Matter of Perspective



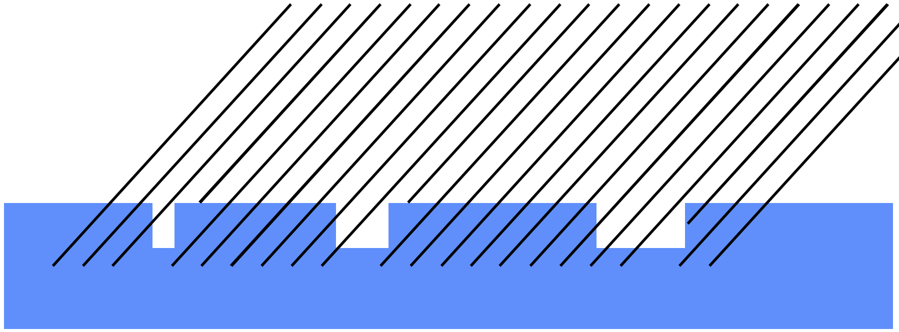


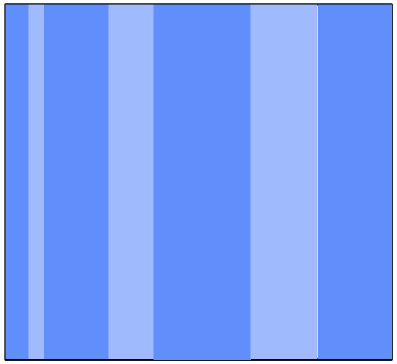
Top View



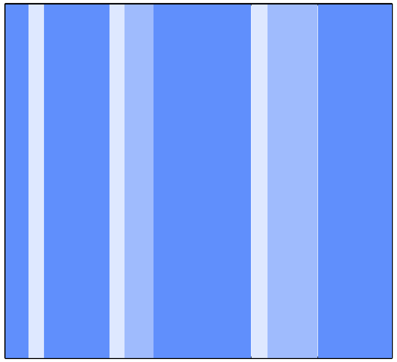
SIMS View

It’s a Matter of Perspective





Top View



SIMS View

Secondary Ion Yield Varies with Primary Ion Angle of Incidence

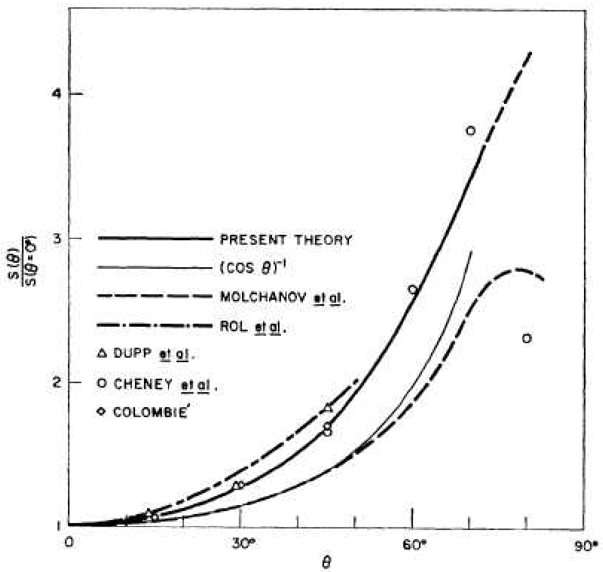


FIG. 11. Variation of the sputtering yield with angle of incidence for Ar^+ ions incident on polycrystalline copper. Thick solid curve: Eq. (74) evaluated for $m=\frac{1}{2}$; thin solid curve: $1/\cos\theta$. Experimental results of Dupp and Scharmann (Ref. 81), Molchanov and Tel'kovskii (Ref. 82), Cheney and Pitkin (Ref. 83), Rol *et al.* (Ref. 84), and Colombié (Ref. 85).

Sigmund, Phys. Rev. 184, **383** (1969).

For polycrystalline and isotropic substances, sputter yield should be:

$$Y(\Theta) / Y(0) = (\cos \Theta)^{-f}$$

Θ = angle of incidence w/respect to surface normal

$Y(0)$ = yield at normal incidence

f depends on M_1/M_2

$M_1/M_2<3$ f~= 5/3

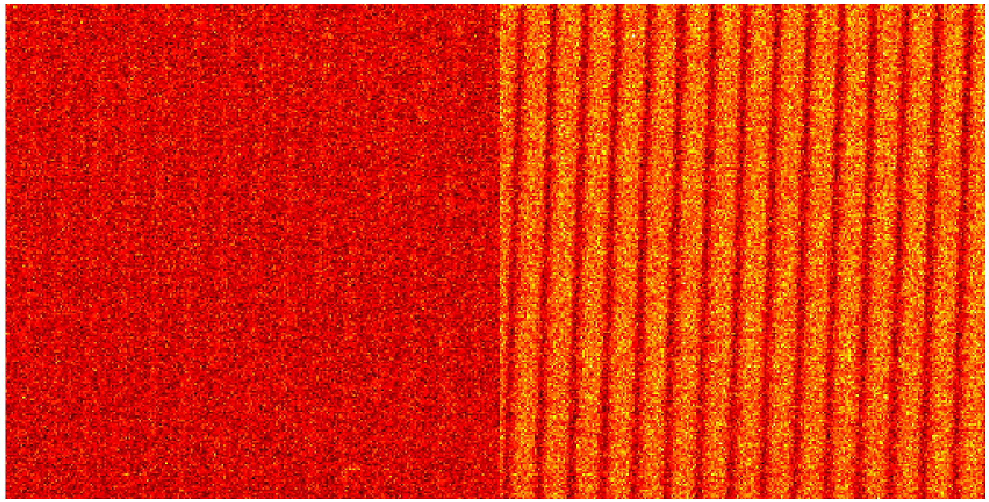
$M_1/M_2>3$ f decreases to <1

Benninghoven, Secondary Ion Mass Spectroscopy, Wiley (1987) p. 193-194.

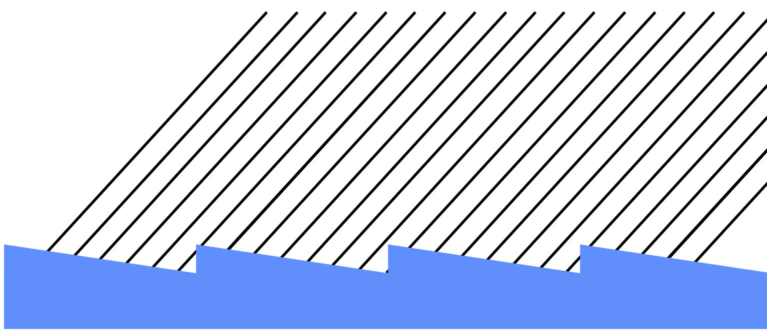
Spectral intensity and shape change with surface angle.

Idealized Surface (grating) Illustrates Issue

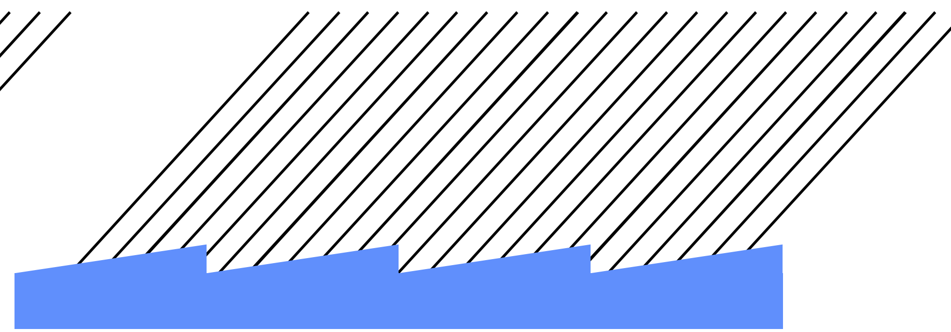
Grating with blaze angle= 8.6º from flat



Rotation=0º Rotation=180º

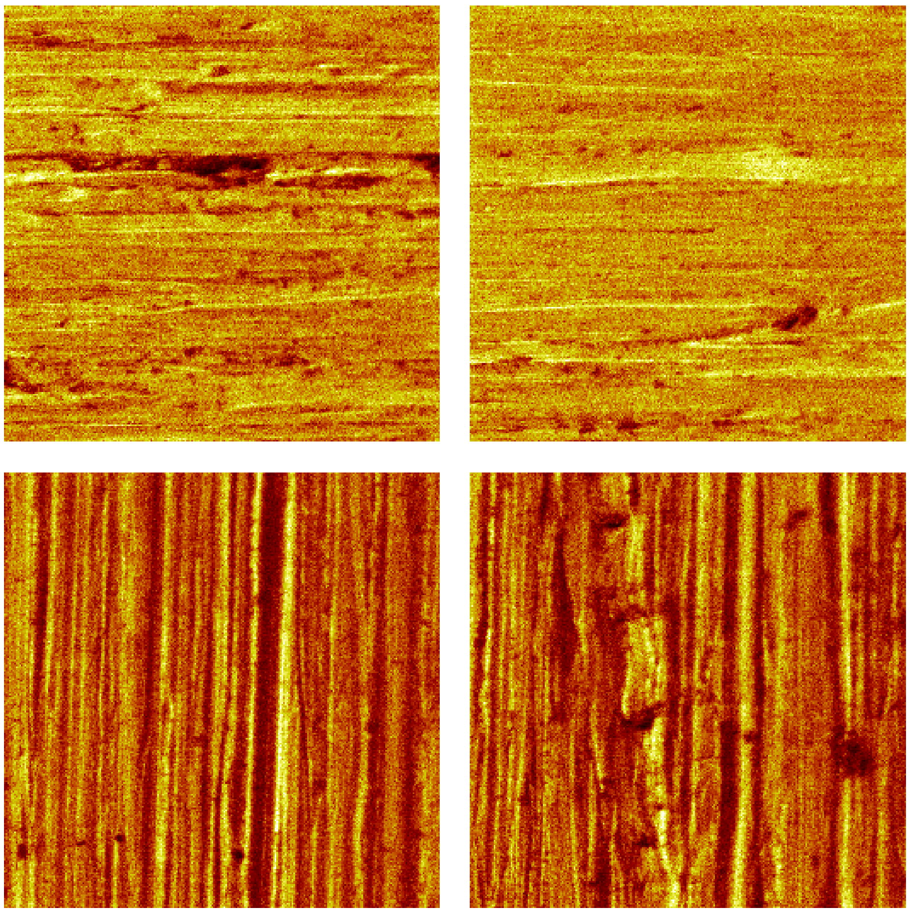


Beam-Surface angle from normal= 36.4º



Beam-Surface angle from normal= 53.6º

Rolled Stainless Steel Surface Illustrates Topographical Influences on Real Data



$100x100 \mu m^2$ area

This is the same sample, just rotated 90 degrees!

With the grain

Against the grain

- What other distortions are Present?
- Is the 'debris' located in the troughs or on the peaks?

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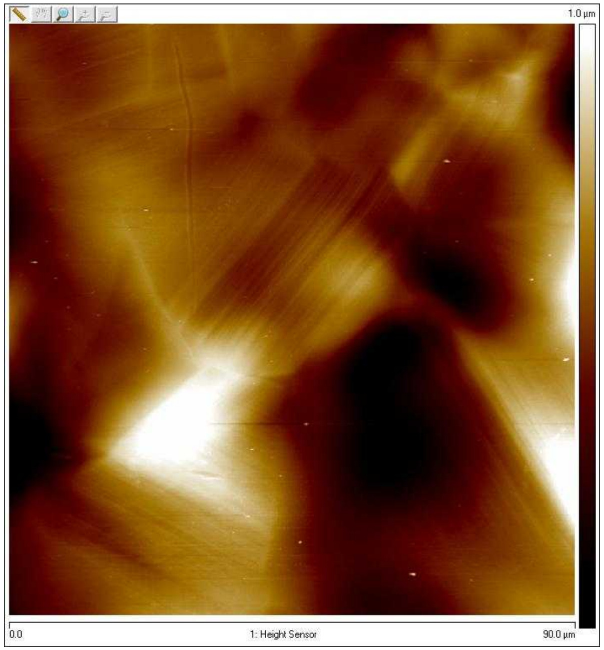
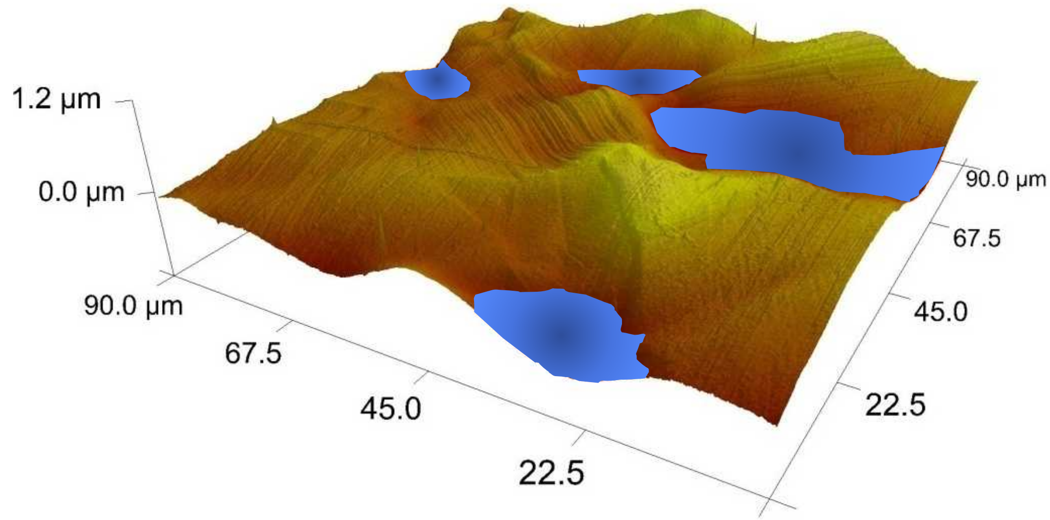
With Accurate Topography, Chemical Information has Relevance





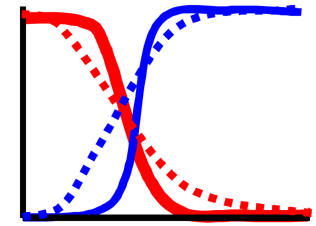
90x90um AFM Height Data

304SS Tensile Test Sample

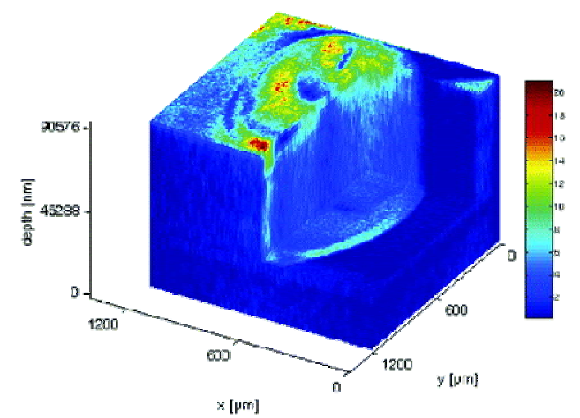
Topography merged with ToF-SIMS chemical information reveals another level of information.

The Problem with 3D Rendering

- **Depth profiles commonly used**
  - **Useful for determining thicknesses of layers and diffusion between those layers**
  - **Many artifacts are seen in systems with non-uniform layers or rough interfaces.**
- **3D analysis**
  - **See lateral distributions of species versus depth.**
  - **Ideal for semiconductor and biological profiling**
- **The Problem:**
  - **Real materials are not typically flat and homogeneous**
  - **Results rendered as idealized cube with flat surfaces (top and bottom especially)**



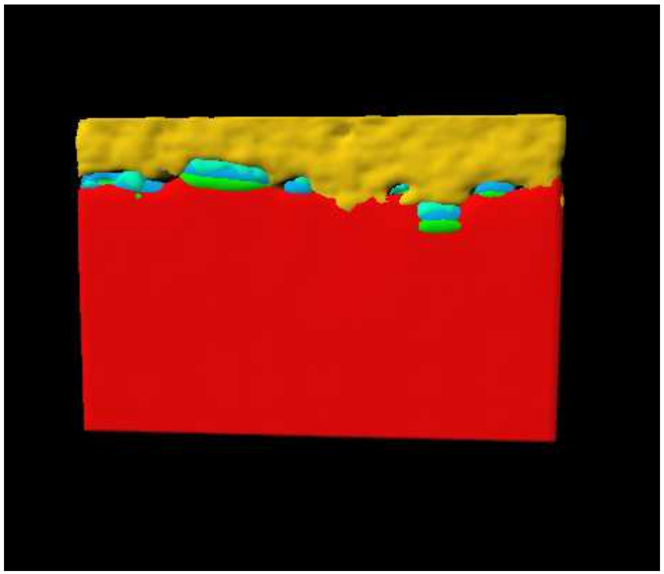
Depth Profile Illustration

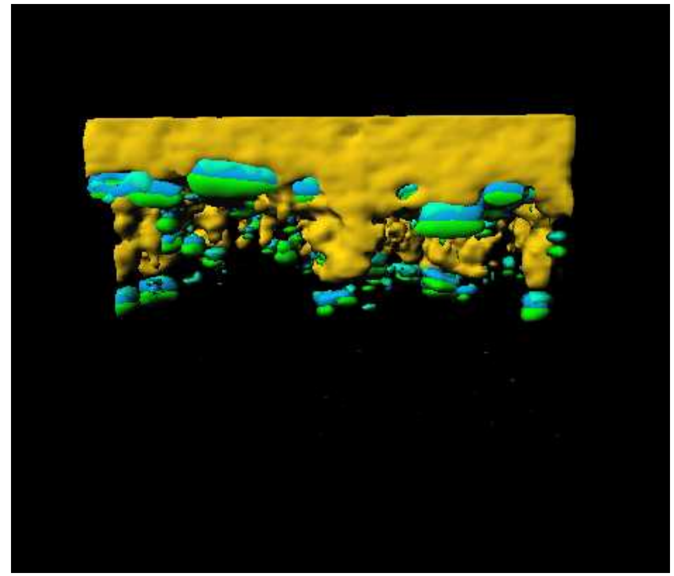


Freeze dried ***Xenopus laevis*** **oocyte**
Fletcher, et. al, Anal. Chem. **2007,** 79, 2199-2206

Goal: Develop methods to correct 3D volume to actual morphology.

ToF-SIMS 3D Analysis Assumes Ideal Cube

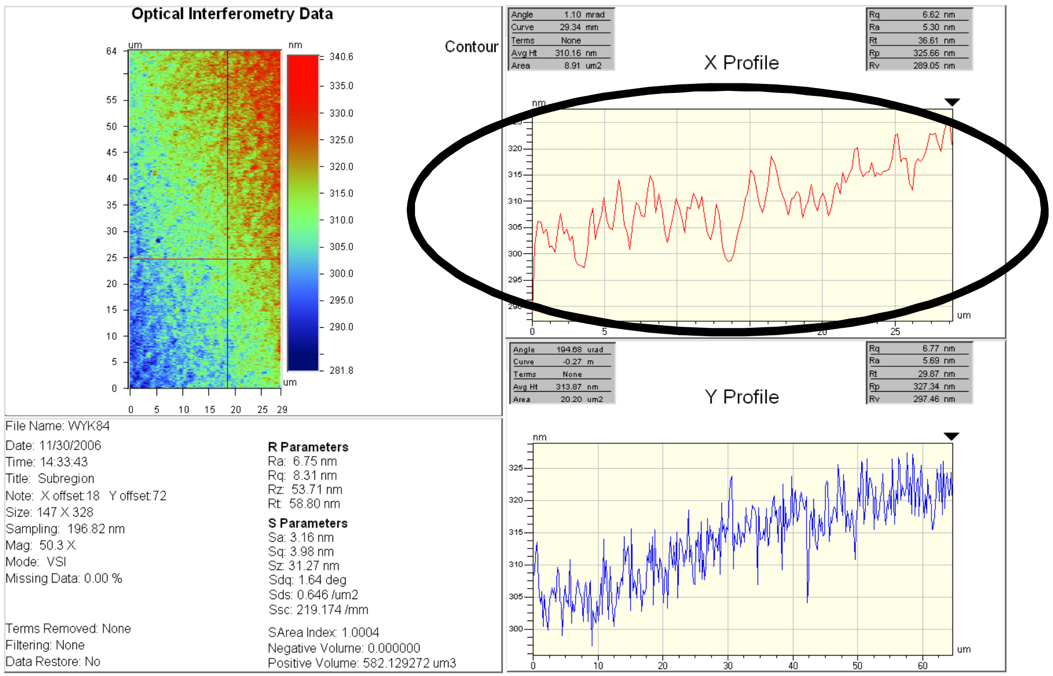


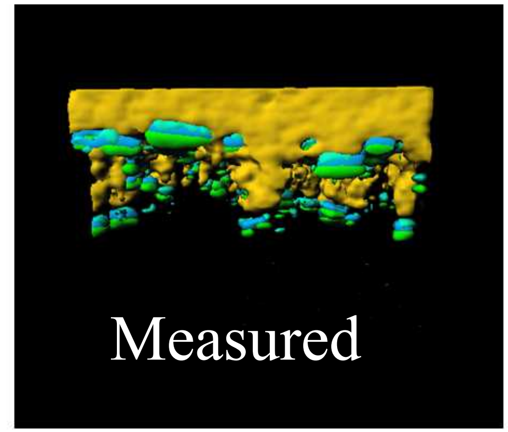


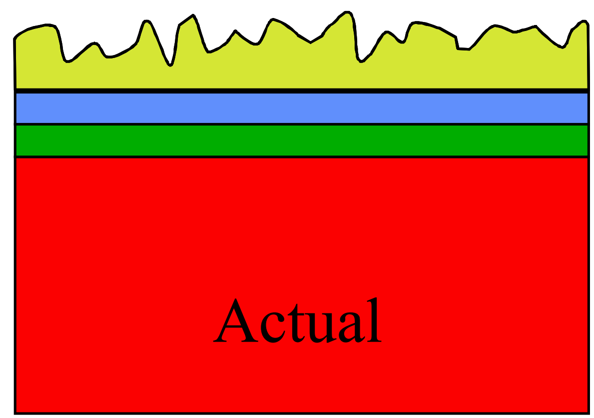
See 4 unique layers on top of a substrate layer (not shown.)

But, is this representation correct?

Standard 3D Rendering Method can be Misleading







The surface layer varies in thickness, leading to an apparent roughening of the interface.

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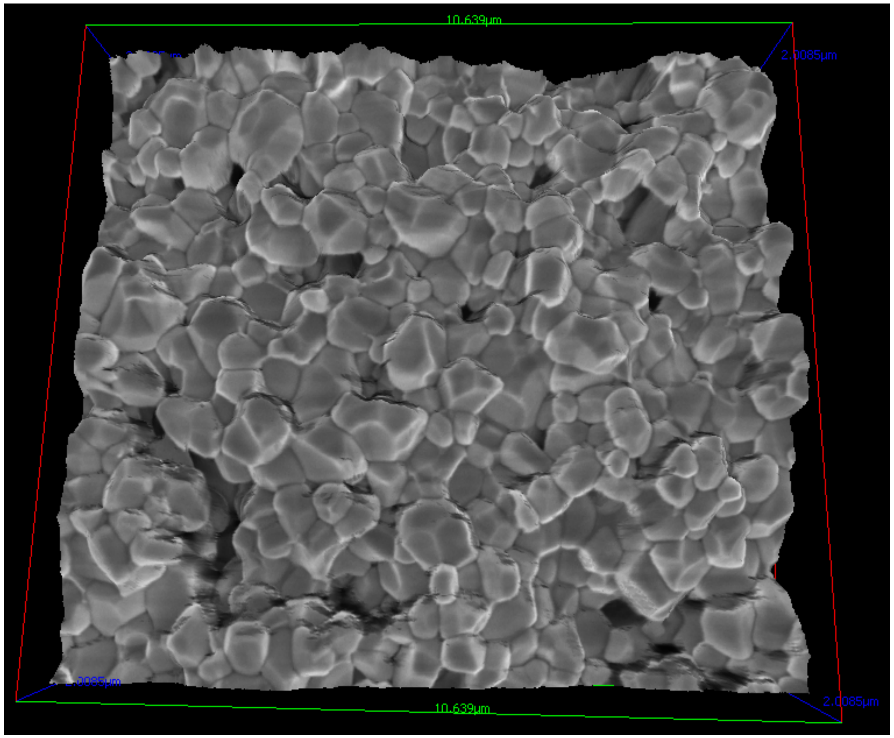
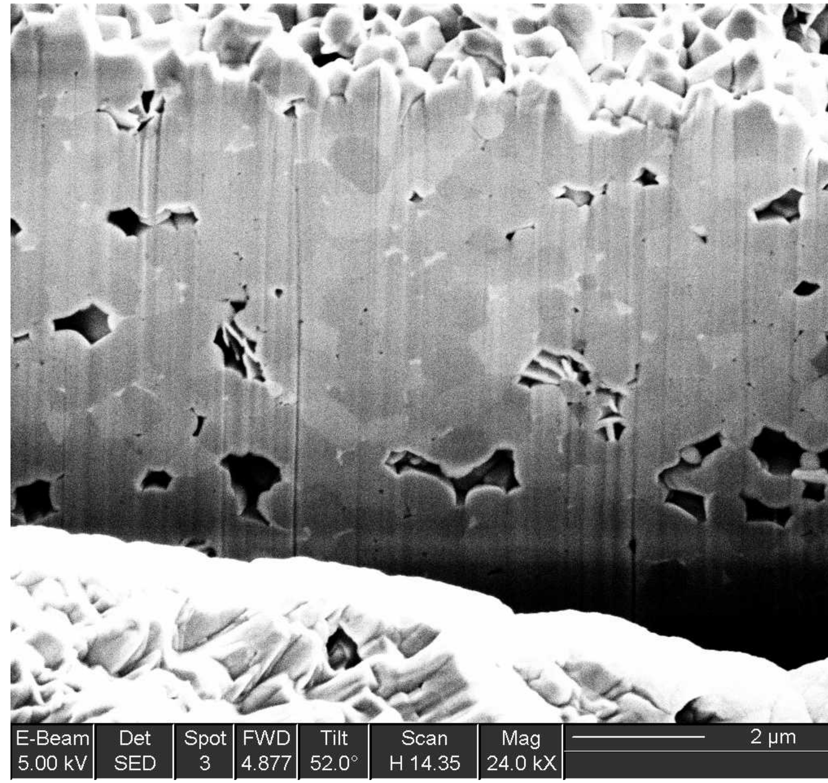
Some Samples are a Lost Cause





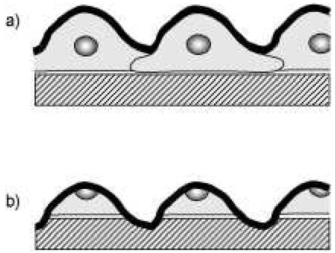
SEM stereo imaging of a $10x10\mu m^2$ area

This material is too complex for accurate 3D measurements.

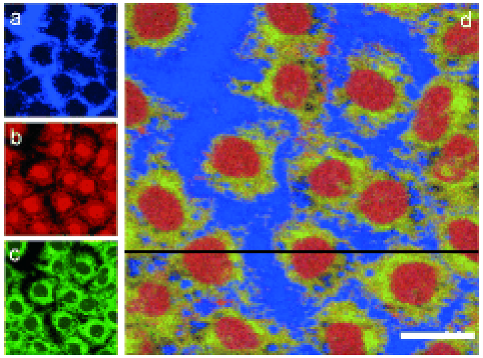
3D Distortion Correction Methodologies

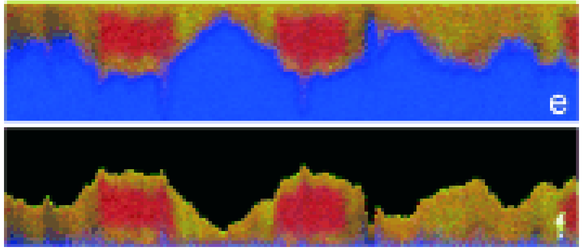
- **No correction, assume perfect cube is correct**
  - Default condition
- **Use a buried interface as a reference**
  - Works when buried interface morphology is known

Normal rat kidney cells grown on glass cover slides.



Breitenstein, et. al., Angew. Chem. Int. Ed. 2007, 46, 5332 –5335

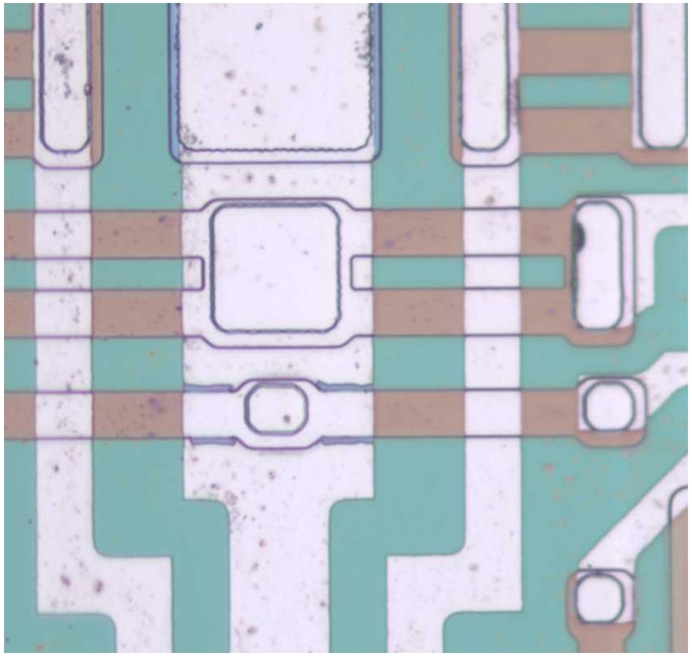


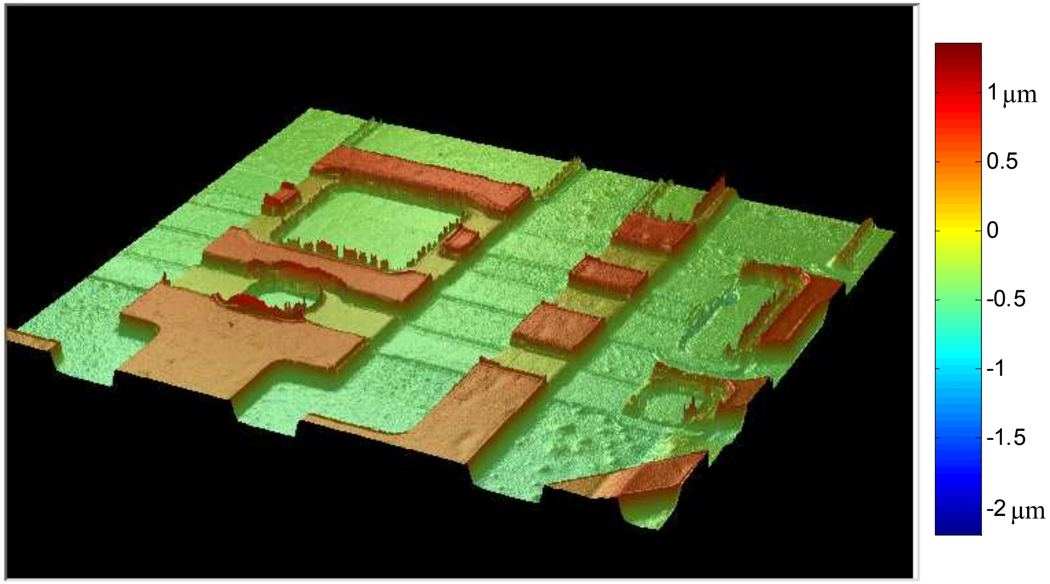


- **Correct the top surface only**
  - Does not correct for roughening.
- **Correct the top and bottom surface**
  - Corrects for roughening

Must know the topography to correct the 3D volume!

Example: 3D Analysis of Semiconductor Device





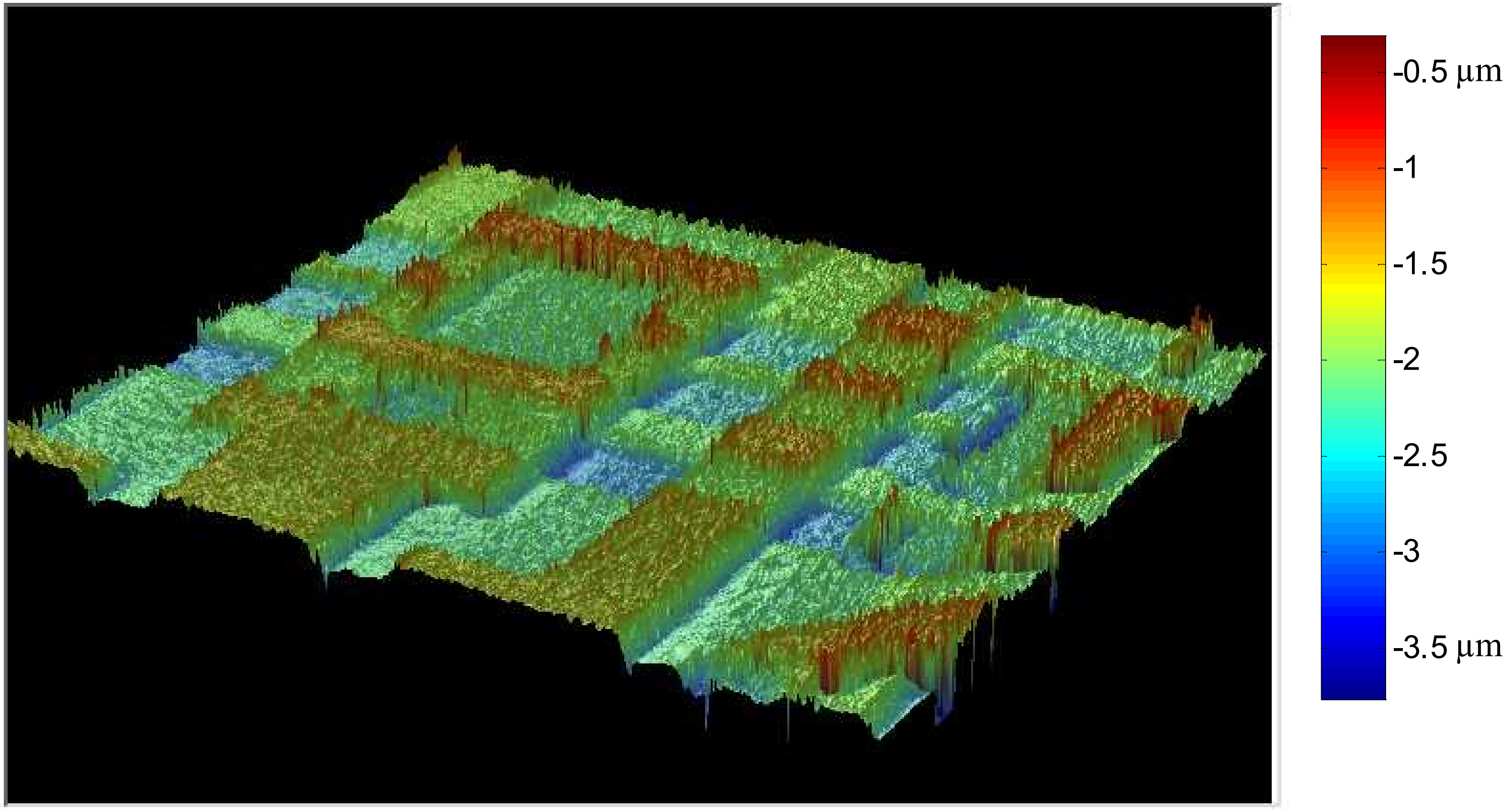
Optical Profilometry of Analysis Region

- Levels show 1-1.5 μm initial height difference, little roughness

Optical Photograph

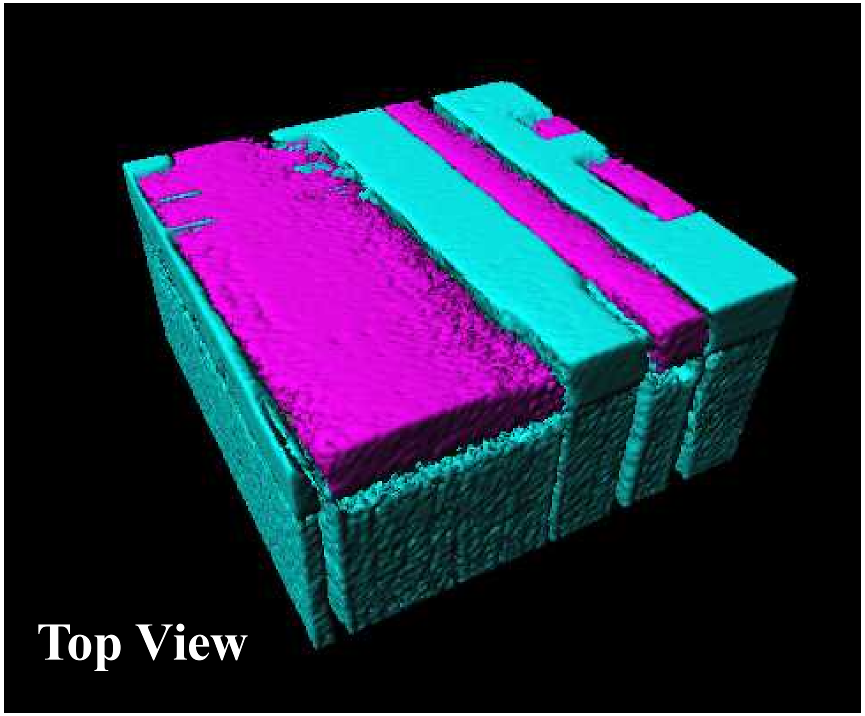
- No morphology can be seen in this view

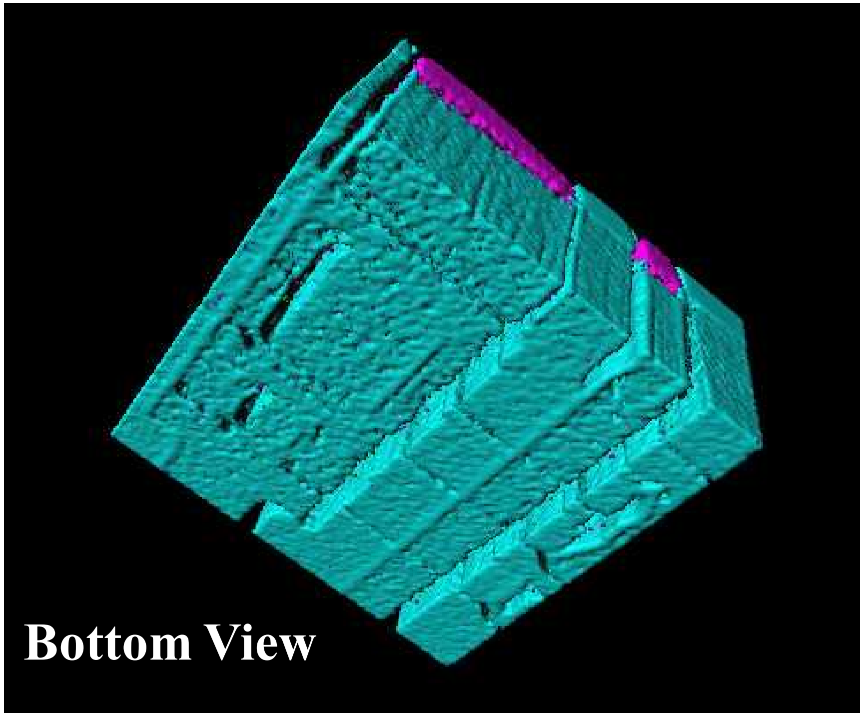
Analysis Region after 2.2µm of Material was Removed



- **Extreme roughness after ion milling**
- **Now levels have about 1.5-2µm height difference**

3D Rendering of Data, As Is





- See Ti-W layer (Magenta) and Si (Cyan)
- Some texturing due to ion yield variations

Wrong Morphology!

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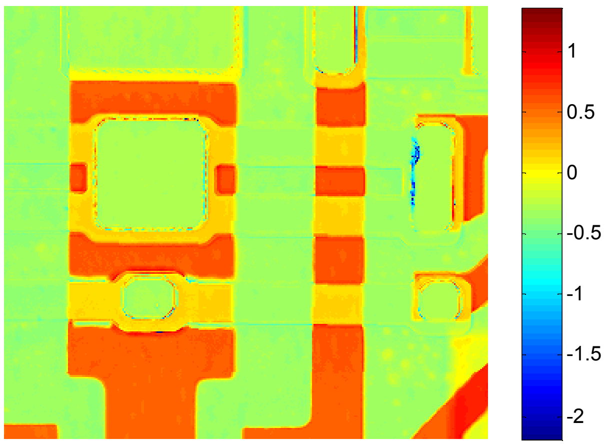
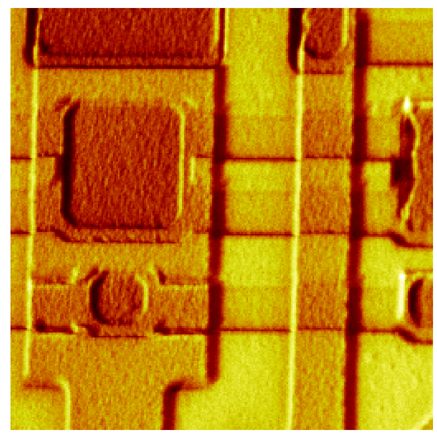
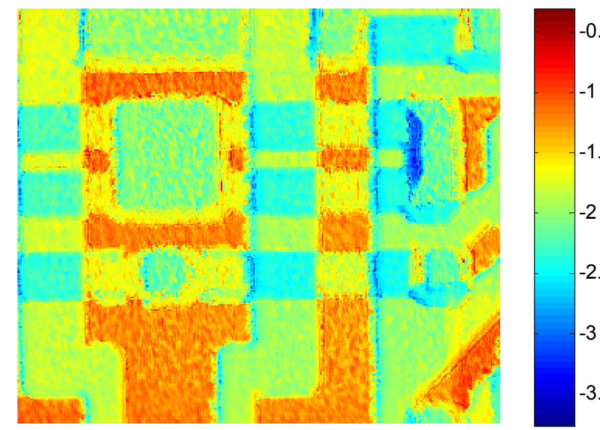
Measured Morphology must be Aligned to Profile Data Before 3D Correction



Before Profile



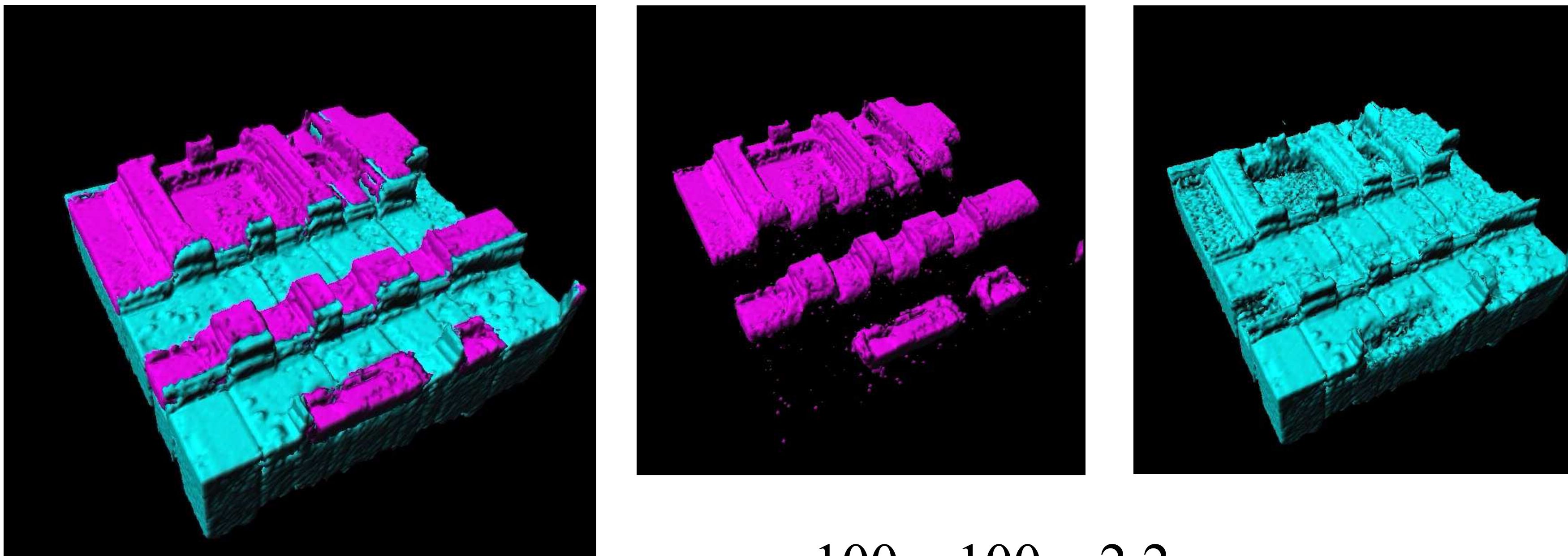
Si image from profile
($100 \times 100 \mu m^2$)



After Profile

Once aligned, 3D volume can be morphed to the correct shape.

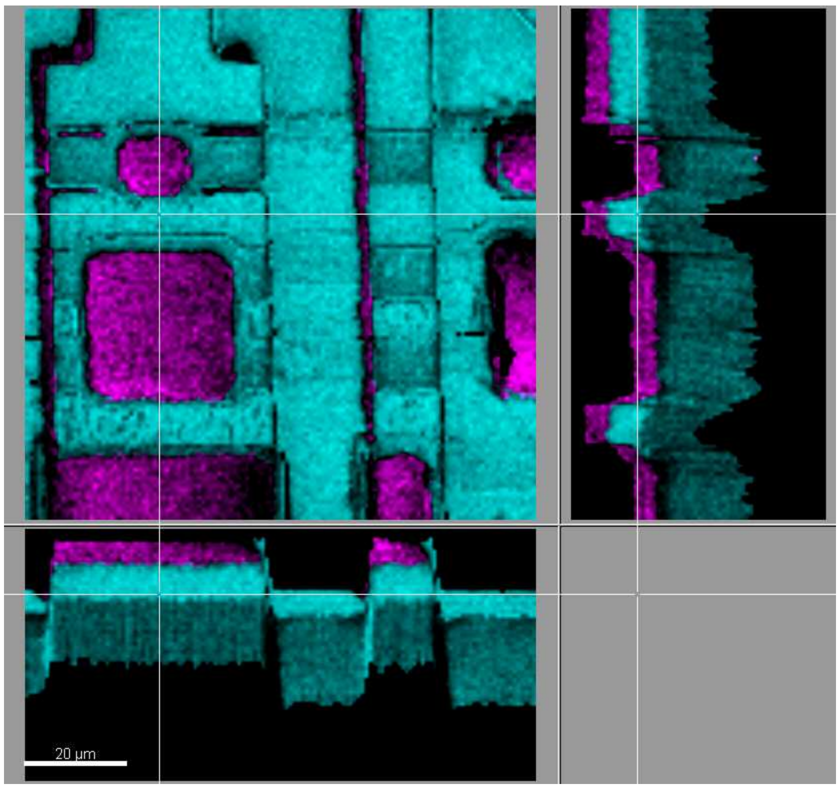
Corrected 3D Volume

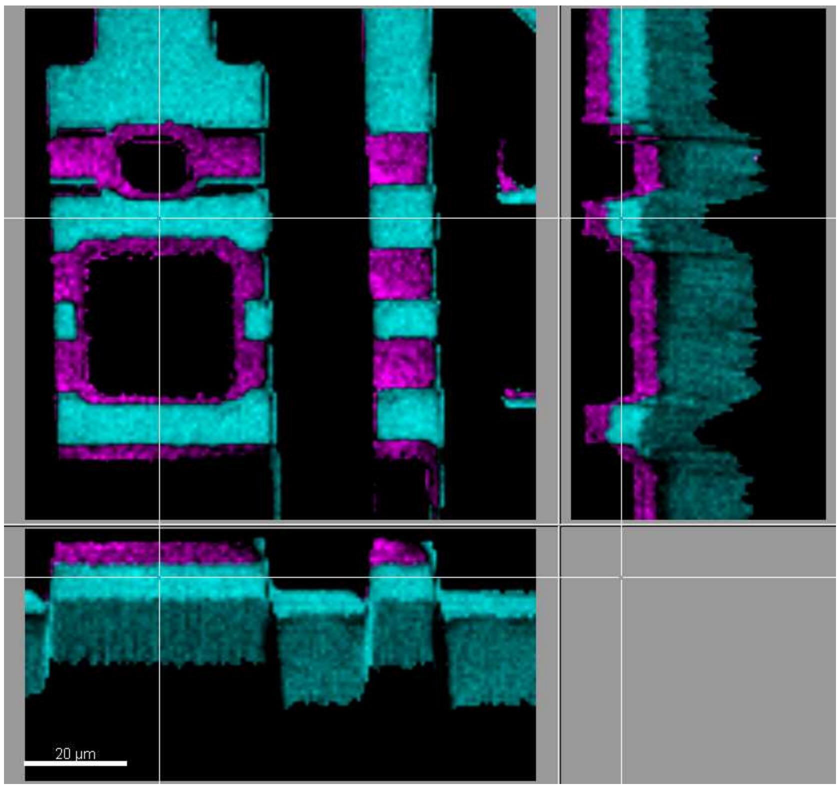


100 x 100 x 2.2 μm

- Now shows correct 3D morphology
- Bottom is corrected for extreme roughness found at crater bottom.

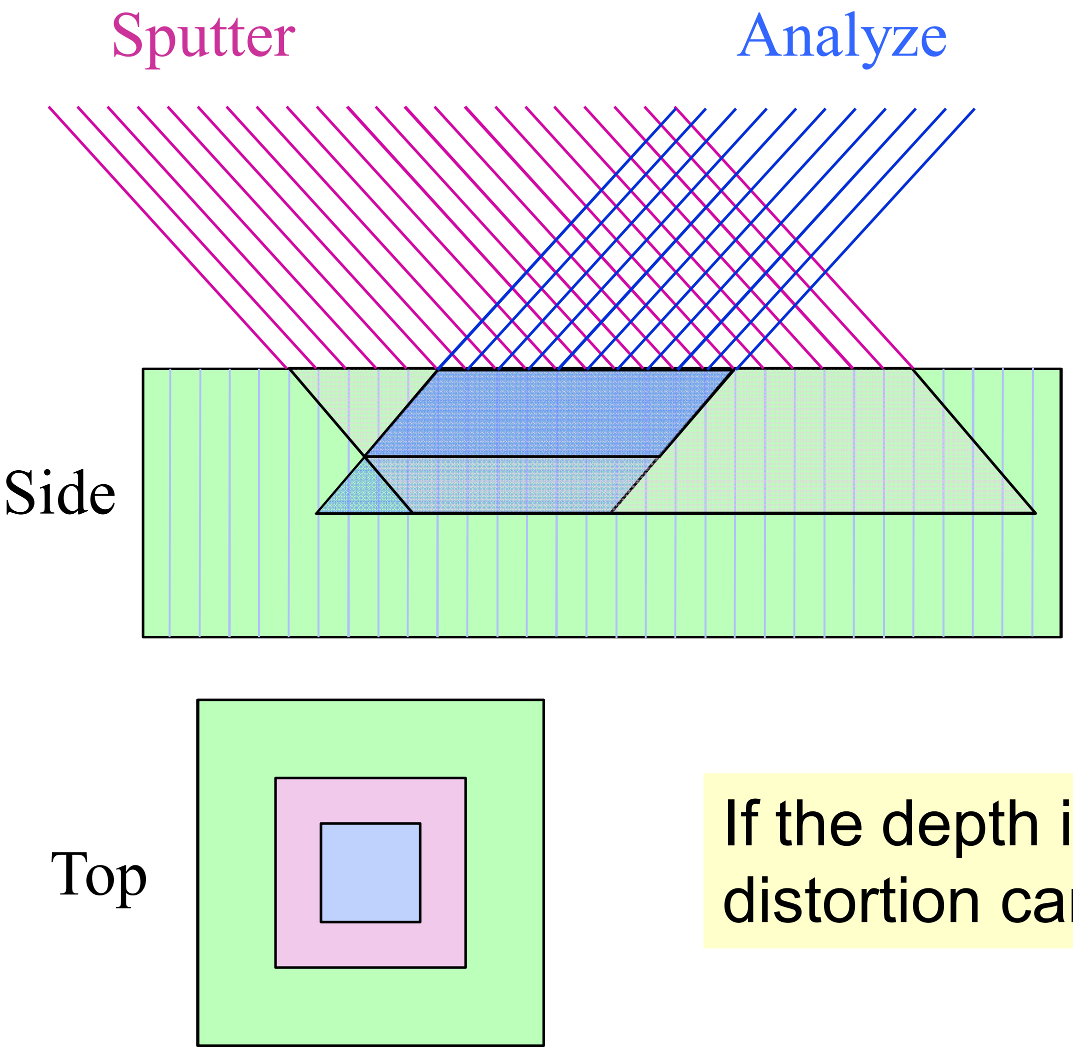
Corrected Volume Cross-sectional Views

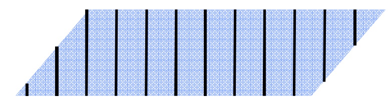




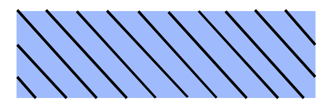
Note: uniform layer of Ti-W overlaying surface

Depth Profiling Has it's Own Analysis-Related Distortions





Actual analyzed volume



Rendered volume without correction

If the depth is known, this distortion can be corrected.

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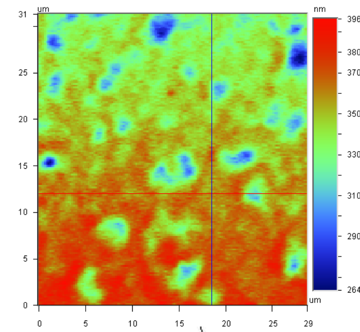
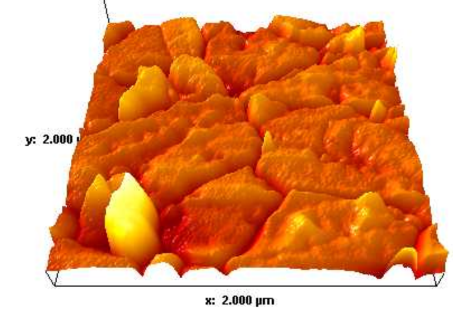
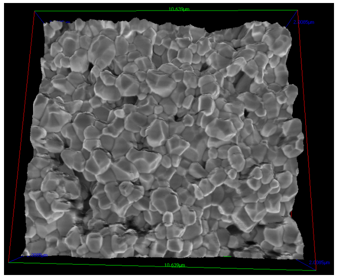
Select an Appropriate Topography Measurement Method

- **Optical Profilometry (Interferometry)**
  - Cannot measure steep regions
  - Diffraction limited (limited at high magnifications)
- **Atomic Force Microscopy (AFM)**
  - Difficult to acquire good quality topographical data
  - Scan head limited (limited at low magnifications-large areas)
- **Stereo Microscopy (SEM)**
  - Can measure very rough surfaces
  - Does not work on smooth or featureless surfaces







Must have good quality topographical data.

Measuring Topography and Aligning to SIMS Data is Very Difficult

- Because accurate high-resolution topography is needed, AFM analysis is preferred.
- It is difficult to match AFM areas with SIMS areas.
- A scheme for accomplishing this is planned.

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Conclusions

- 2D ToF-SIMS image analysis can be difficult to interpret without understanding and correcting topography.
- Topography can lead to many different distortions and contrast mechanisms.
- One must be careful when performing 3D analysis as rendered volume may be distorted
  - Surface topographical features
  - Buried roughness
  - Roughness caused by ion milling
- One can correct 3D rendering under certain conditions using several methods.
- Still need good way to accurately measure the topography of a surface, then measure it in the ToF-SIMS.

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