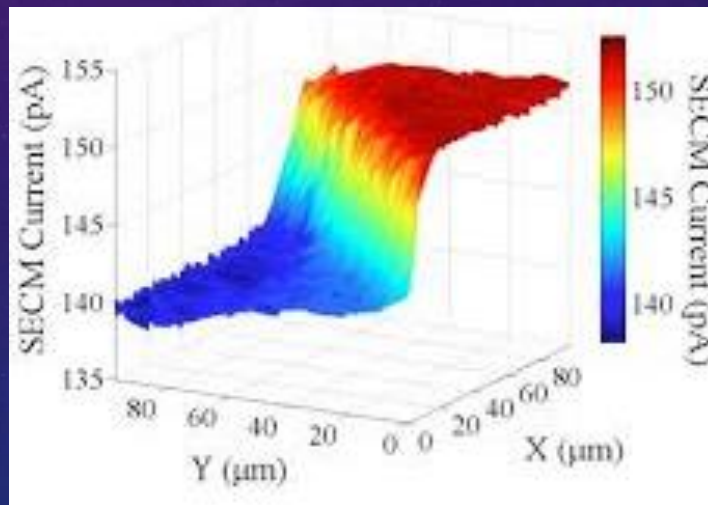


# SCANNING ELECTROCHEMICAL MICROSCOPY



PRESENTED BY:

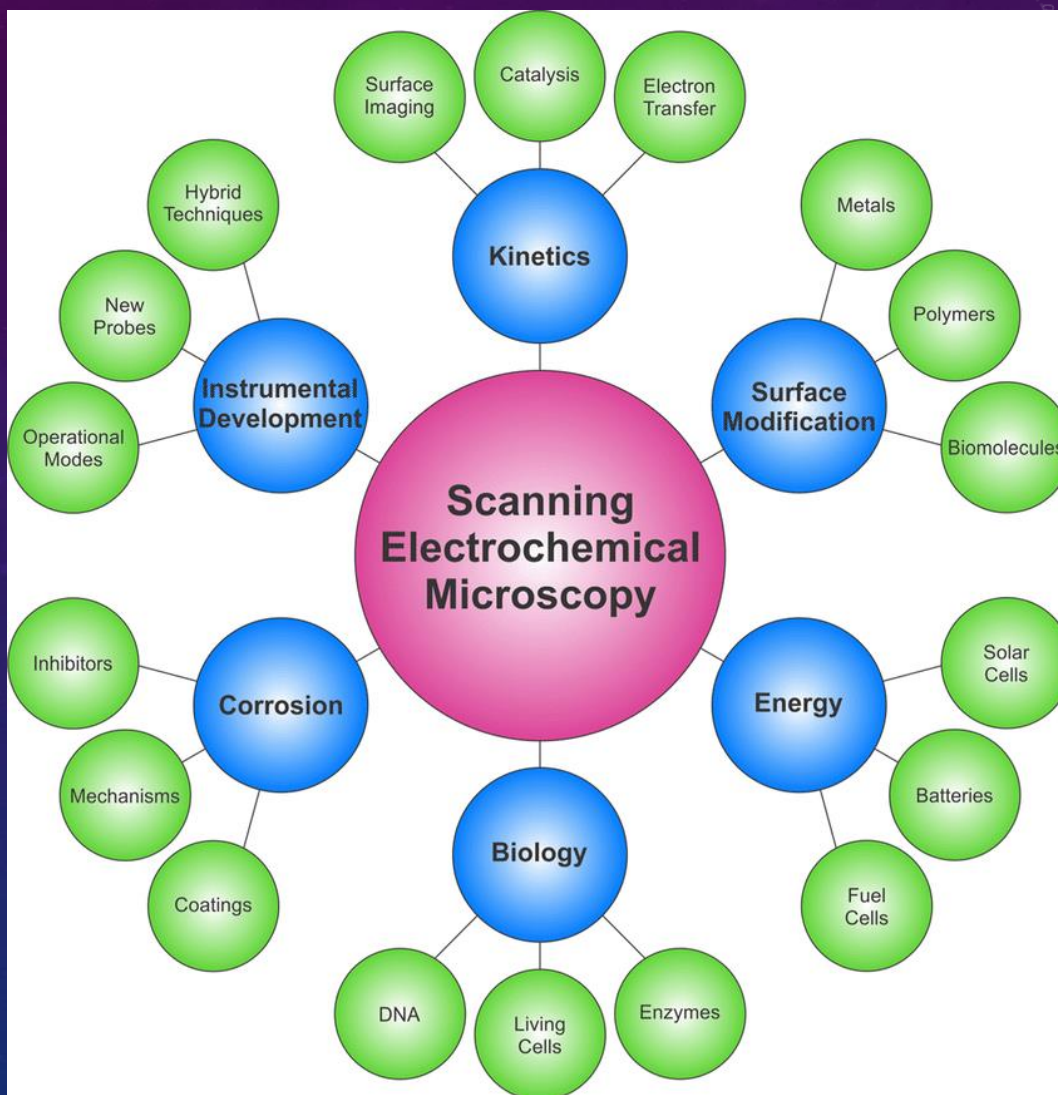
**NOBUHLE NDEBELE**

# BACKGROUND

- Introduced by Bard and Engstrom simultaneously in the 1980s
- Electroanalytical scanning technique
- Quantitative technique
- Analyses the activity, morphology and topography of interfaces
- Monitors electric current flowing through the tip of a small electrode when scanned across a substrate
- The response depends on:
  - ✓ surface topography and
  - ✓ electrochemical activity



# APPLICATIONS



# COMPONENTS

- Bipotentiostat
- 3D Positioning system
- SECM tip (small scale probe)
- Computer

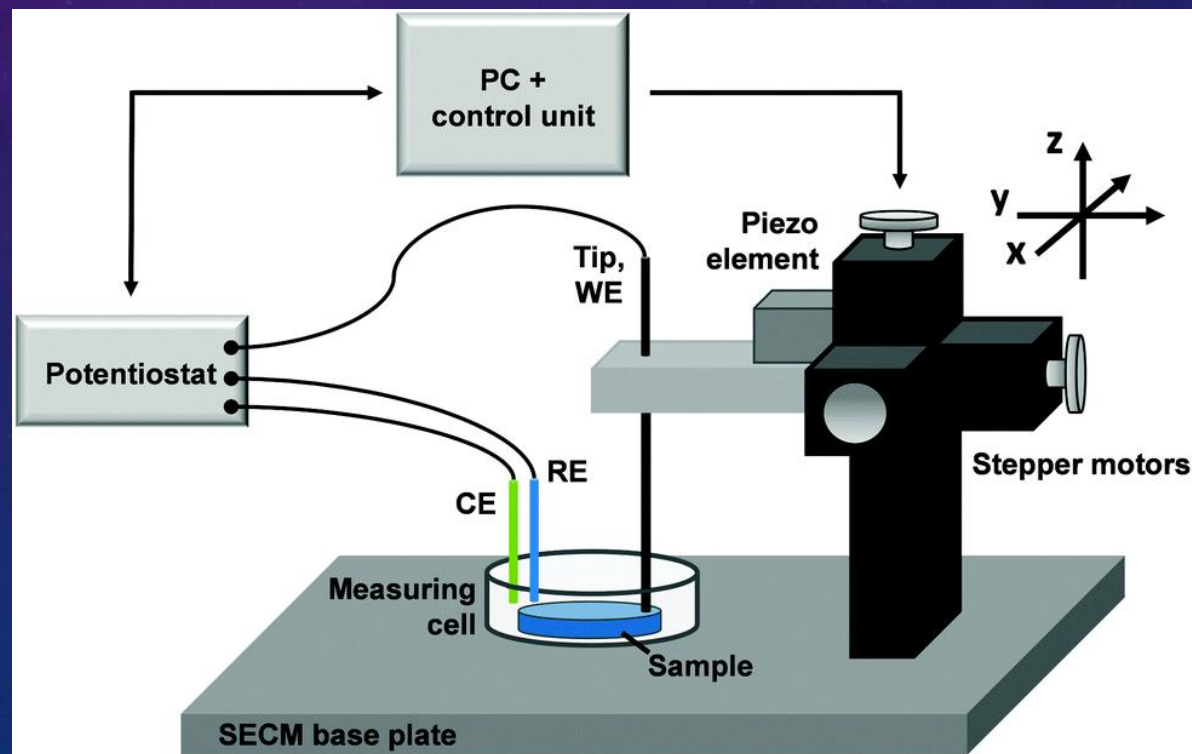


Image adapted from:  
E. Ventosa and W.  
Schuhmann. *Phys  
Chem Chem Phys.*  
2015, , 17, 28441—  
28450.





# ADDITIONAL COMPONENTS

- Optical microscope
- Fluorescence detection system
- Constant distance unit



# PROBE



- Ultramicroelectrode (UME)  $< 25 \mu\text{m}$
- Measurements depend on the dimensions of the probe (micrometer to nanometer)
  - ✓ fast steady-state response
  - ✓ Low electrical potential difference
- Probe selection depends on process under investigation
  - ✓ Amperometry
  - ✓ Potentiometry



# PROBES

- Amperometric probes

- ✓ 99%
- ✓ Highly robust
- ✓ Ease in probe positioning
- ✓ Fast response times (ms-ns)
- ✓ Low selectivity

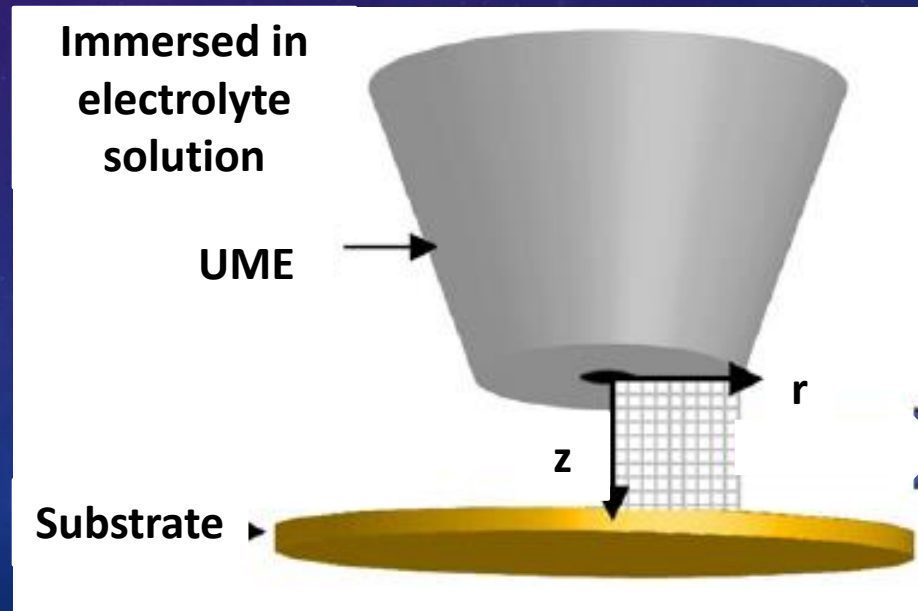
- Potentiometric probes

- ✓ 1%
- ✓ Small lifetime
- ✓ Highly sensitive
- ✓ Slow response time (ms-s)
- ✓



# MODES OF OPERATION

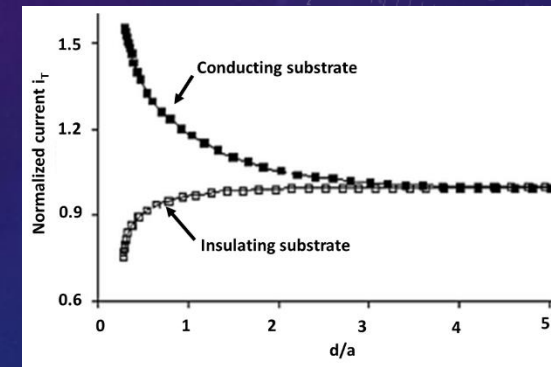
- Tip generation/ tip collection mode
- Feedback potentiometric mode
- Redox competition mode
- Direct mode





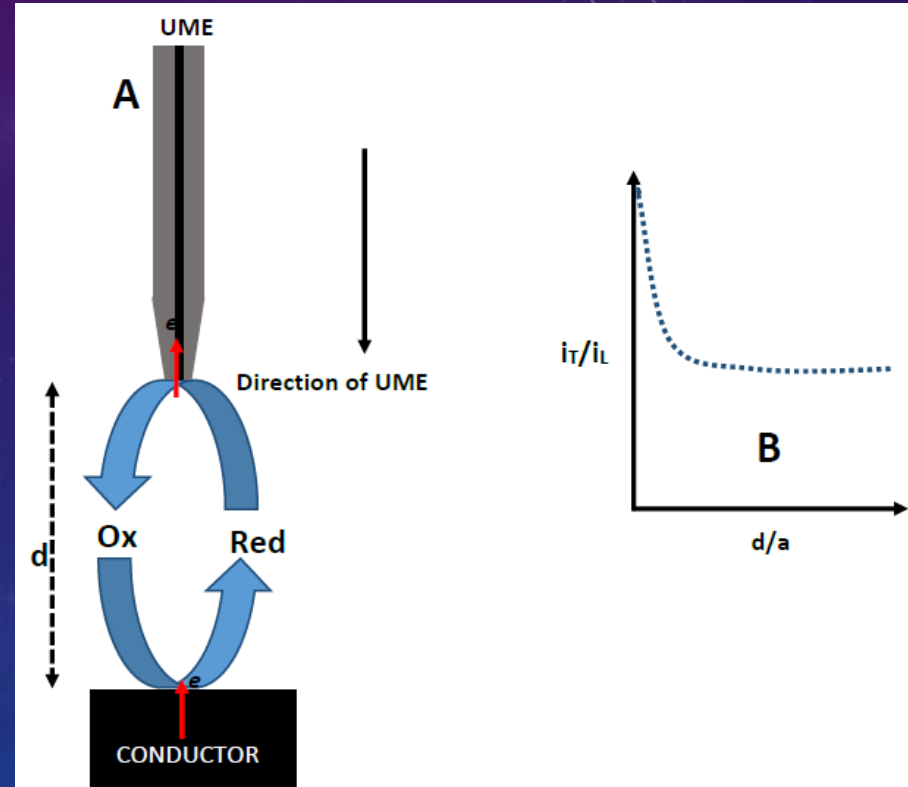
# FEEDBACK MODE PRINCIPLE

- Measures changes in tip current as the UME approaches the substrate in the presence of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox mediators
- Potential is applied
  - ✓ Oxidation:  $\text{Fe}^{2+}/\text{Fe}^{3+}$
  - ✓ Rate: Diffusion of  $\text{Fe}^{2+}$  to the UME tip surface
- ✓ Tip close to conducting surface:  $\text{Fe}^{3+}$  diffuses to the substrate (reduced)
  - ✓ Increase in  $\text{Fe}^{2+}$  generation at the tip = increase in tip current
- ✓ Tip close to insulating surface:  $\text{Fe}^{3+}$  diffusion is hindered
  - ✓ Decrease in  $\text{Fe}^{2+}$  at the tip = decrease in tip current



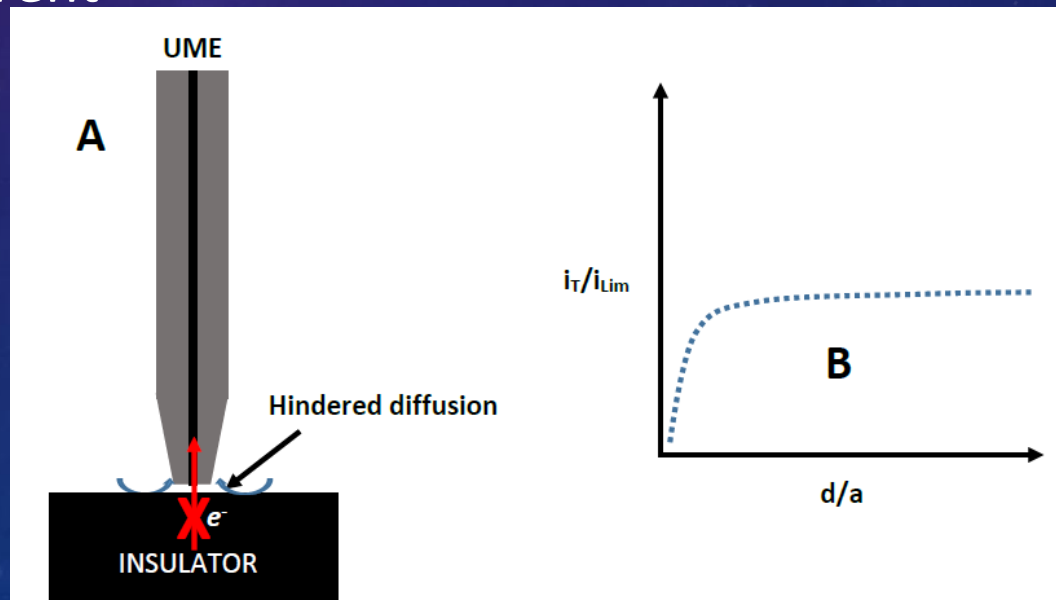
# POSITIVE FEEDBACK

- **Positive feedback**
  - ✓ UME approaches conductive surface
- Large tip-substrate distance
  - ✓ Tip current: mass transfer
  - ✓ Current observed: limiting current
- Reduced tip-substrate distance
  - ✓ Faradaic current increase
  - ✓ Increase in tip currents

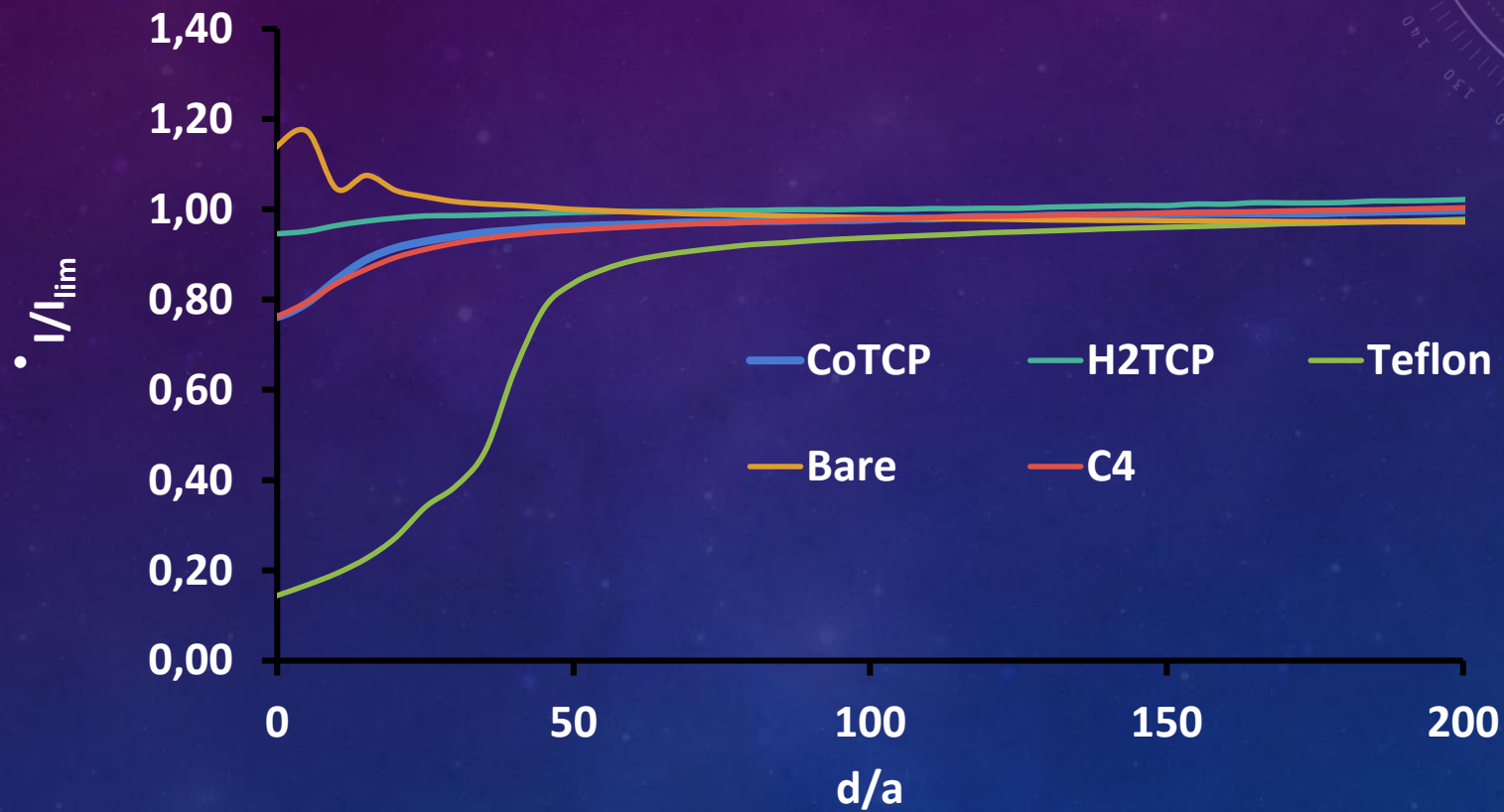


# NEGATIVE FEEDBACK

- Negative feed back
  - ✓ UME approaches non-conductive surface
  - ✓ Diffusion of the redox species to the UME tip is hindered
  - ✓ Current decreases
  - ✓ Decrease in tip current

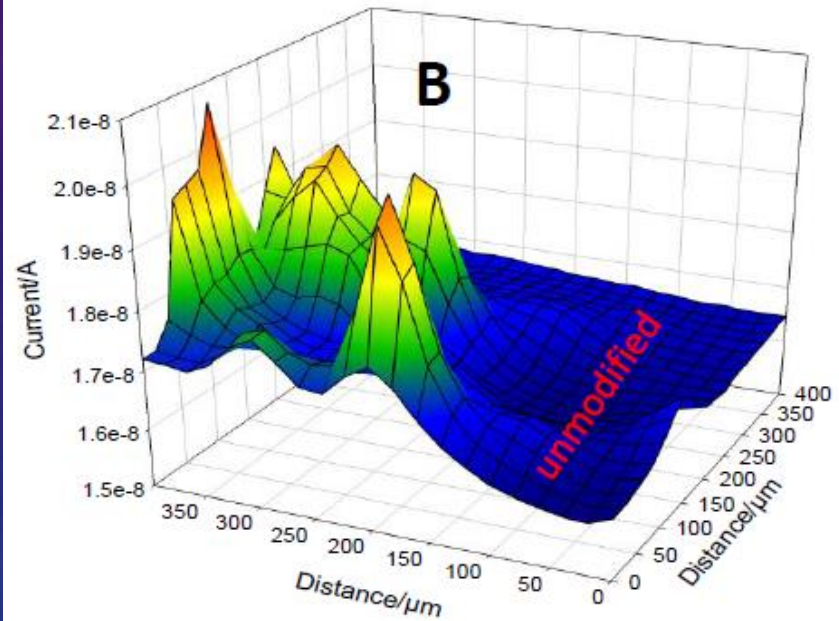
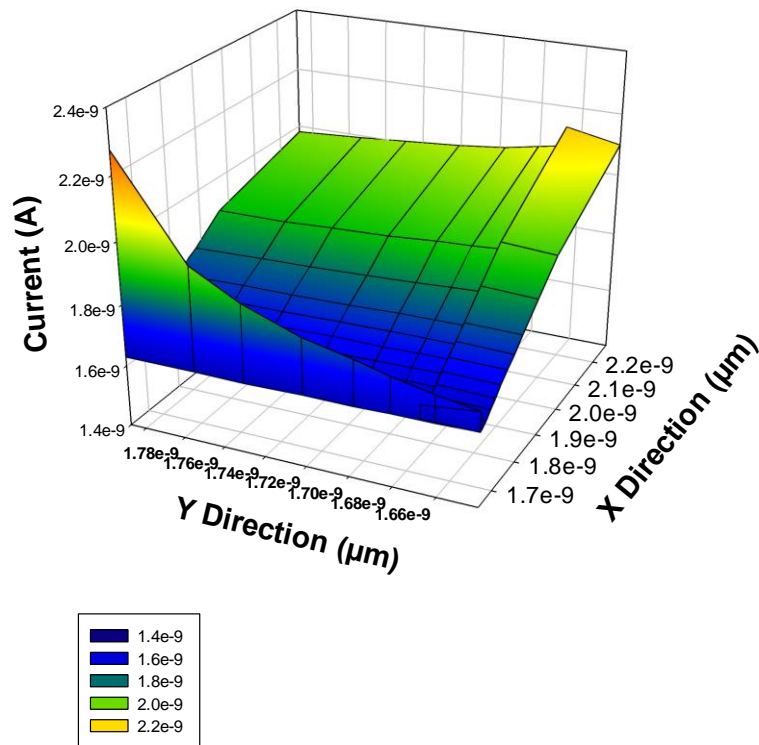


# ANALYSIS





# ANALYSIS



# ACKNOWLEDGMENTS

❖ Family

❖ NRF

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❖ S22 Colleagues 😊 😊 😊

