EMISSION PROPERTIES OF PtSi-COATED SILICON NANOCONES IN THE TRANSITION REGIME

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UNIVERSITY OF TWENTE.

MESA+ INSTITUTE

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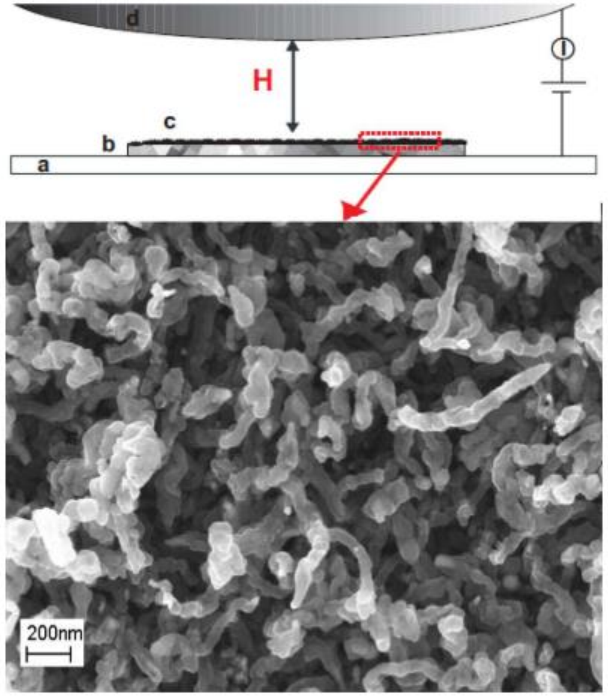
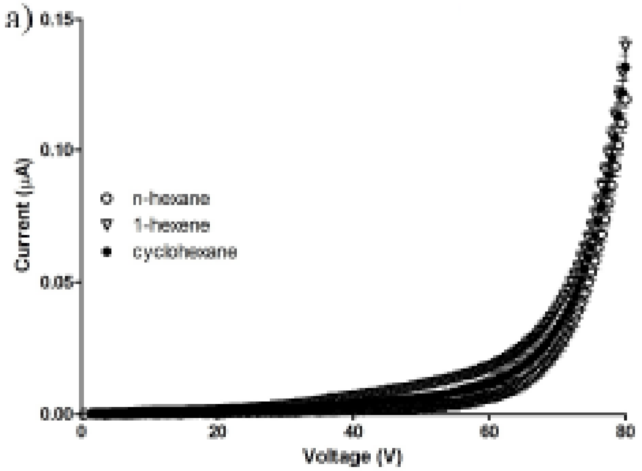
- Motivation
- Fabrication overview
- Experimental setup
- Results

Motivation

Using a field emitter for performing chemical reactions



A. Ağiral, et al., “Charge injection from carbon nanofibers into hexane under ambient conditions,”, 2011.



Solvent type	9,10-dihydroanthracene %	anthraquinone %
Apolar (with or without proton donator)		
n-hexane	None	None
n-hexane + 5%$_{vol}$ ethanol	None	None
n-hexane + 10%$_{vol}$ ethanol	None	1.2
n-hexane + 25%$_{vol}$ ethanol	None	4.3

M. (2016). Morassutto, “Flow chemistry using field electron emission from SiNW’s.,” in *Cold field emission in microreators to perform chemical reactions*, 2016

Fabrication Overview

General process flow: Additive hybrid Lithography

Legend

Silicon

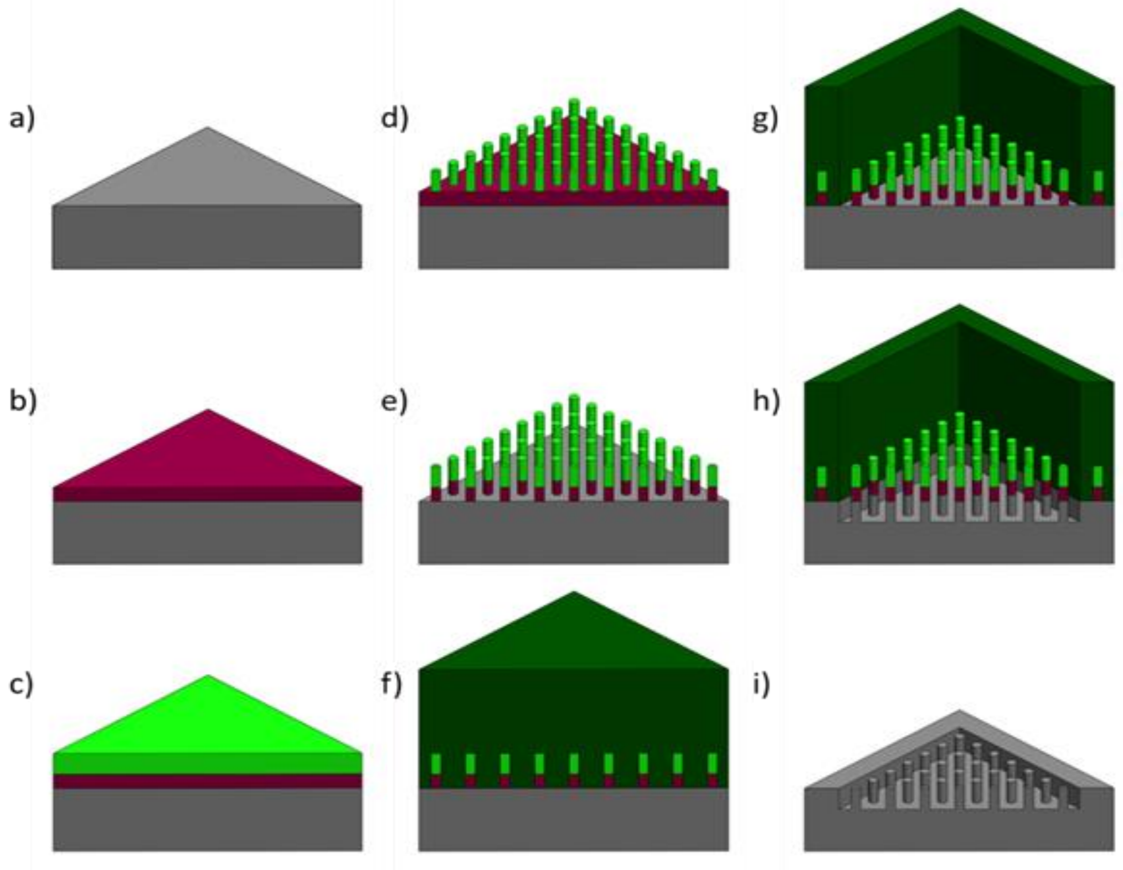
BARC

PFI 88A

OiR 907

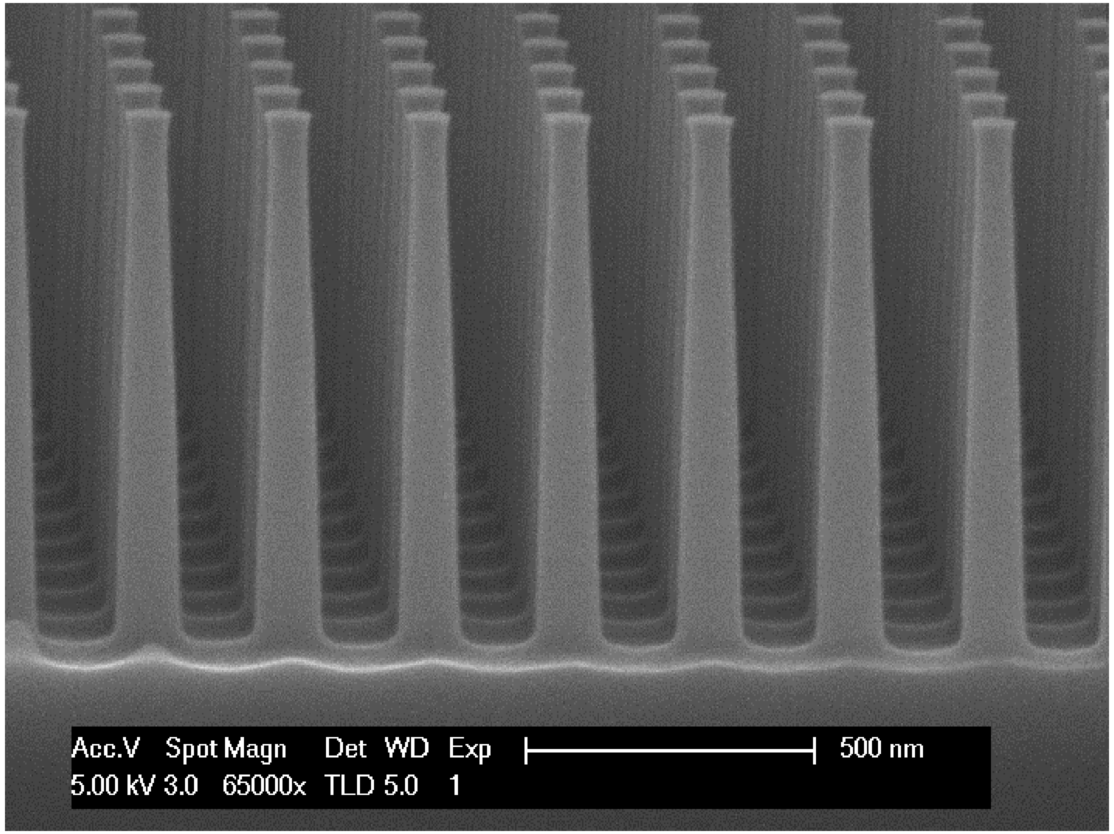
Key features

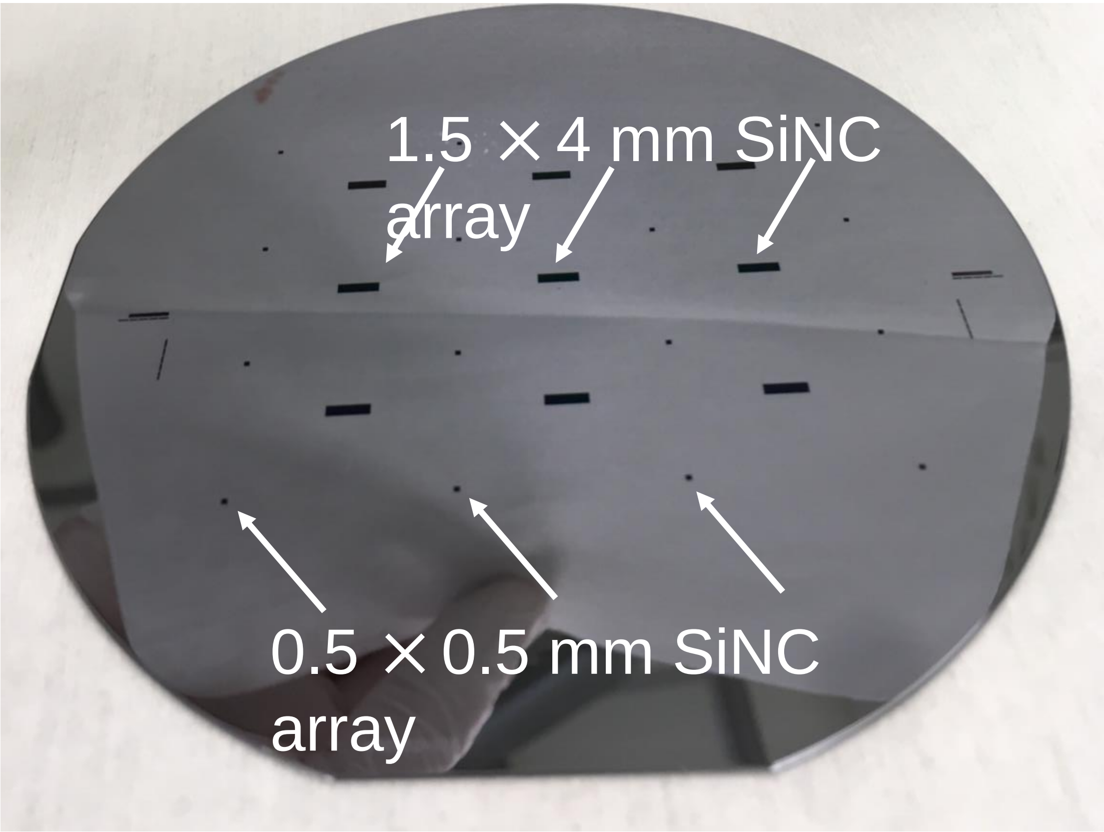
- Combination of conventional and Displacement Talbot photolithography techniques to form etch mask.
- Yields nanoscale patterning at the macroscale.
- Continuous mode reactive ion etching for smooth sidewalls (no scallops)
- Platform for field emitter electrodes device integration



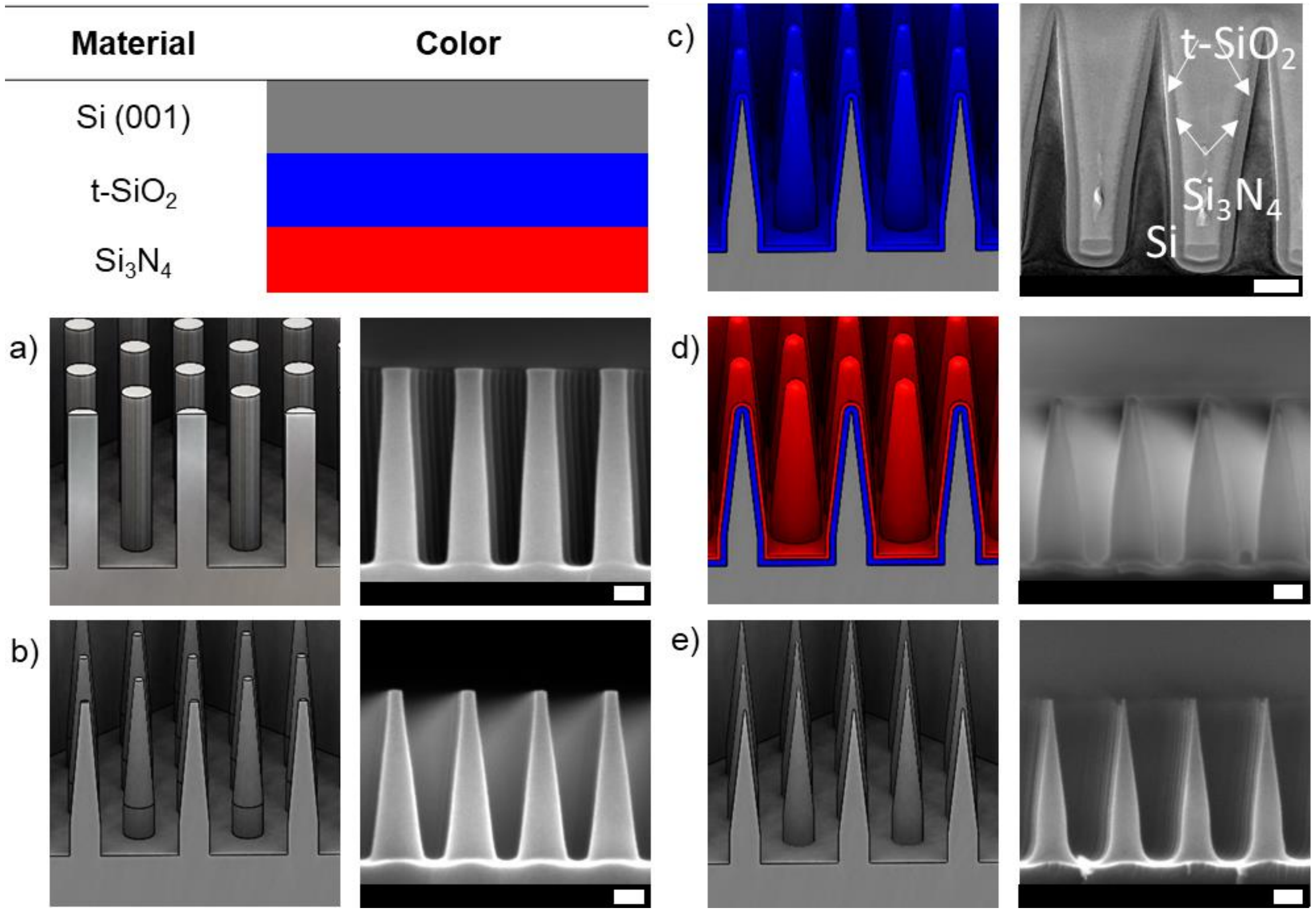
D. Jonker et al.*'Wafer-scale fabrication and modification of silicon nano-pillar arrays for nanoelectronics, nanofluidics and beyond'.* Int. J. of Nanotechnology *(2020)*

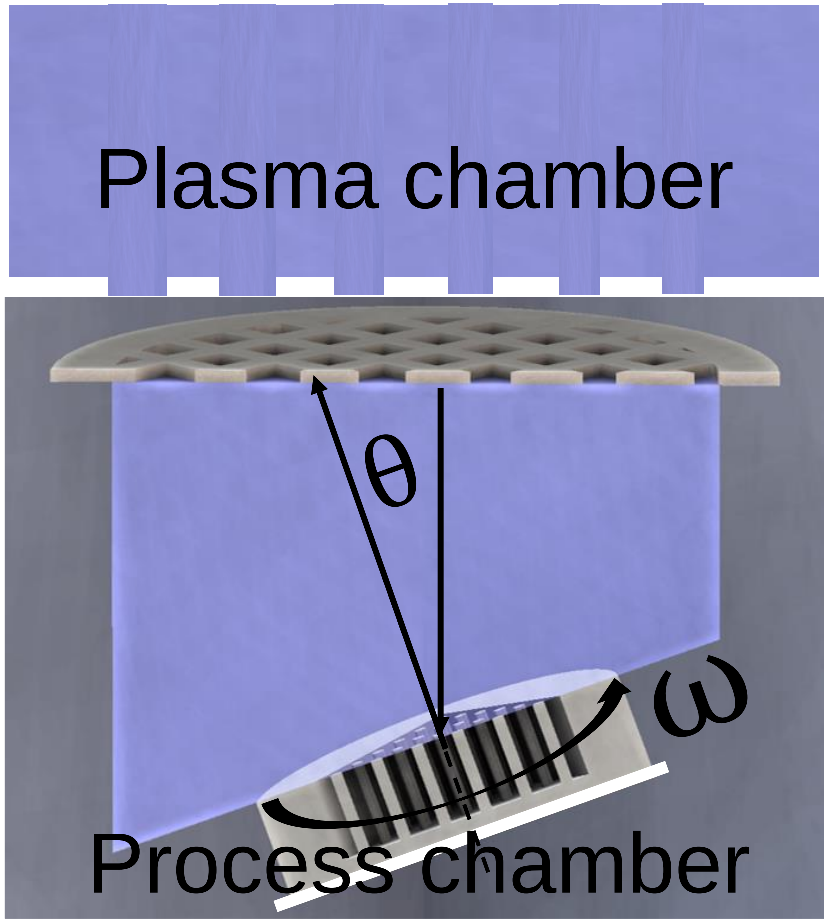
General process flow:
reactive ion etching of silicon





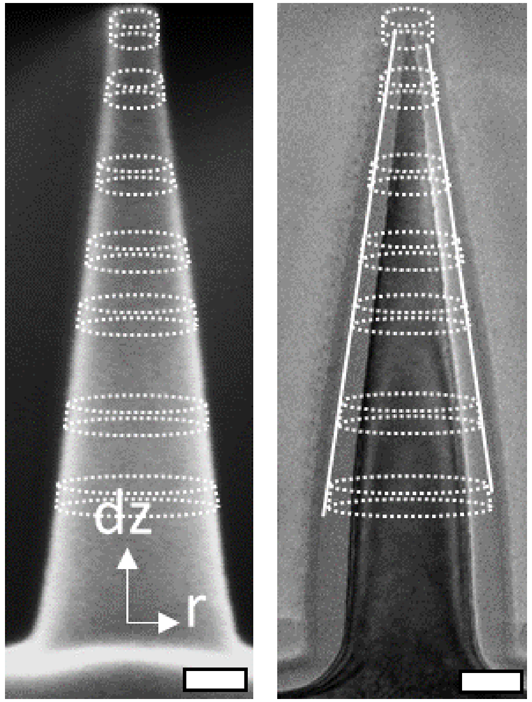
Fabrication of silicon nanocones

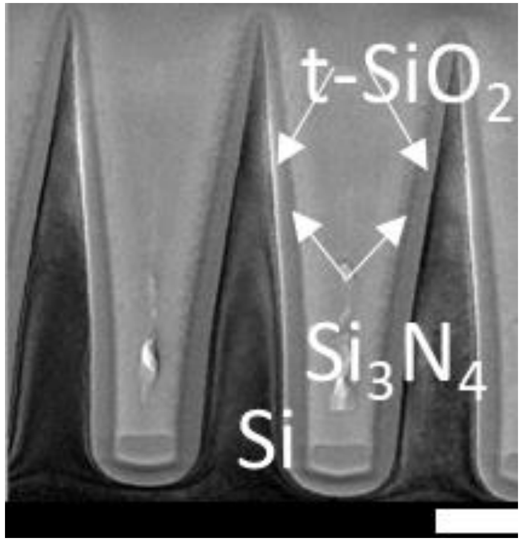




Tapered Oxide thickness

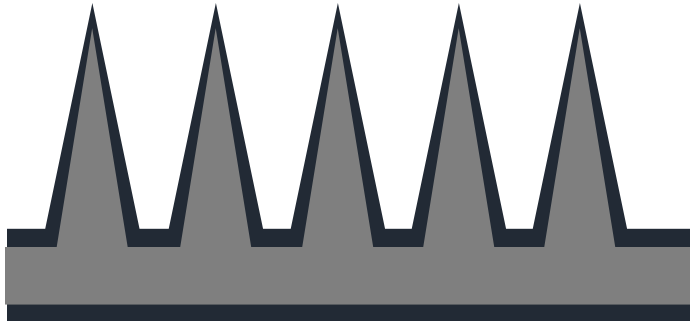
- Gradient oxide thickness along the cone slant
- Oxide thickness ~20 nm at the bottom and ~5 nm at the apices.



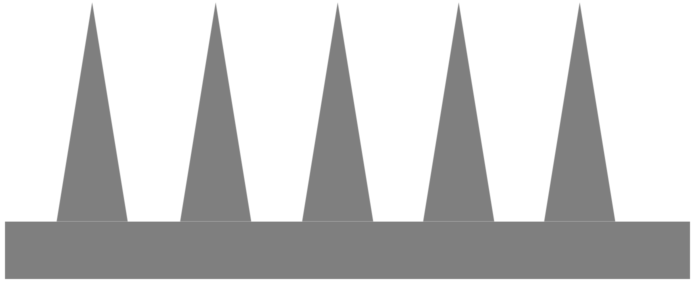


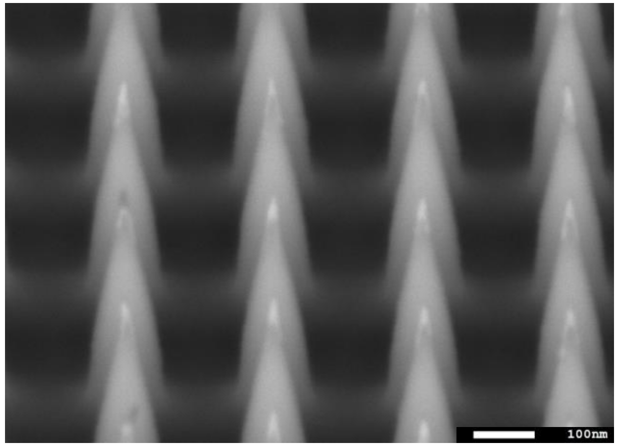
Formation of PtSi on Silicon Nanocones

1. Silicon nanocones with silicon dioxide



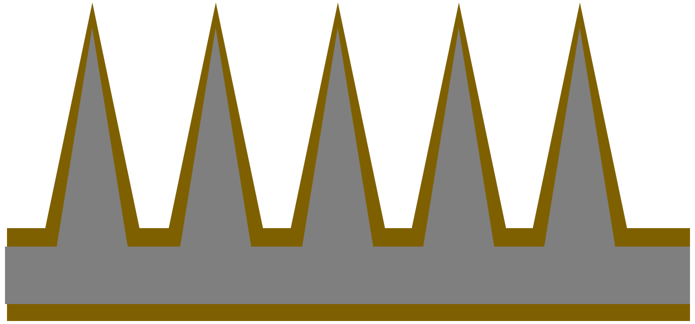
2. Etching of silicon dioxide

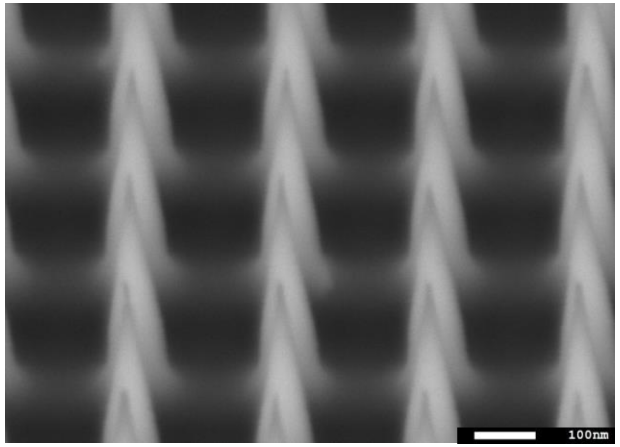




3. Sputter deposition of Platinum

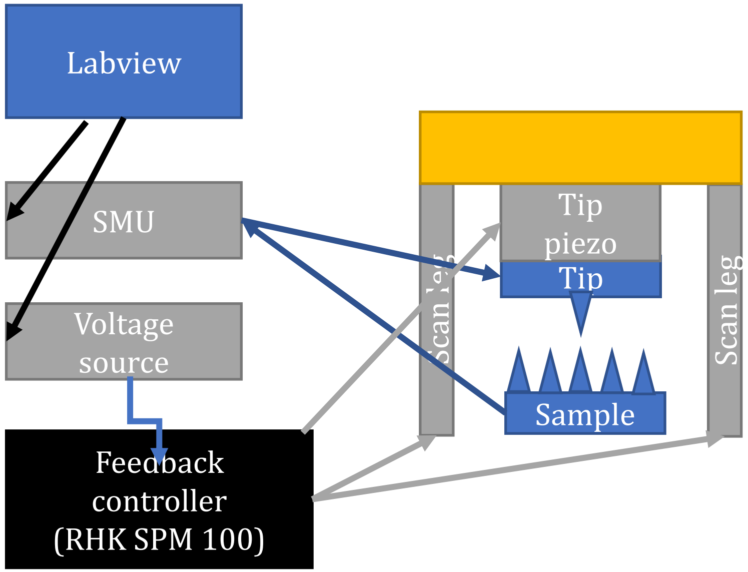
4. Rapid thermal annealing forming Platinum Silicide

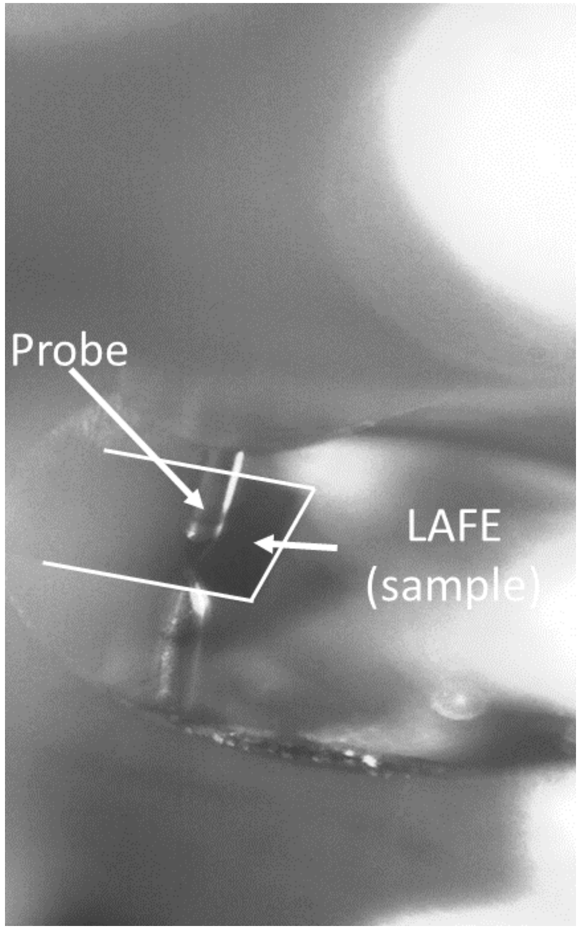


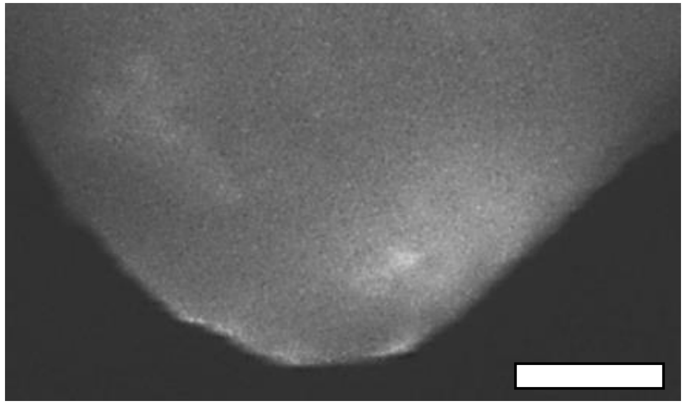


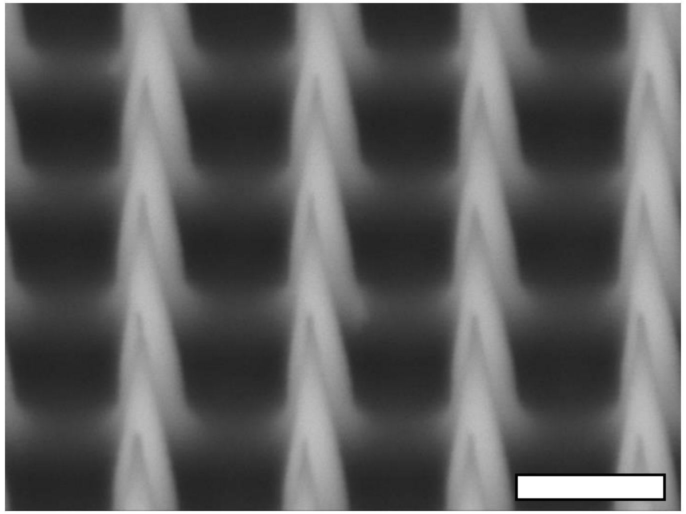
Experimental Setup

Scanning tunneling microscope (Probe)





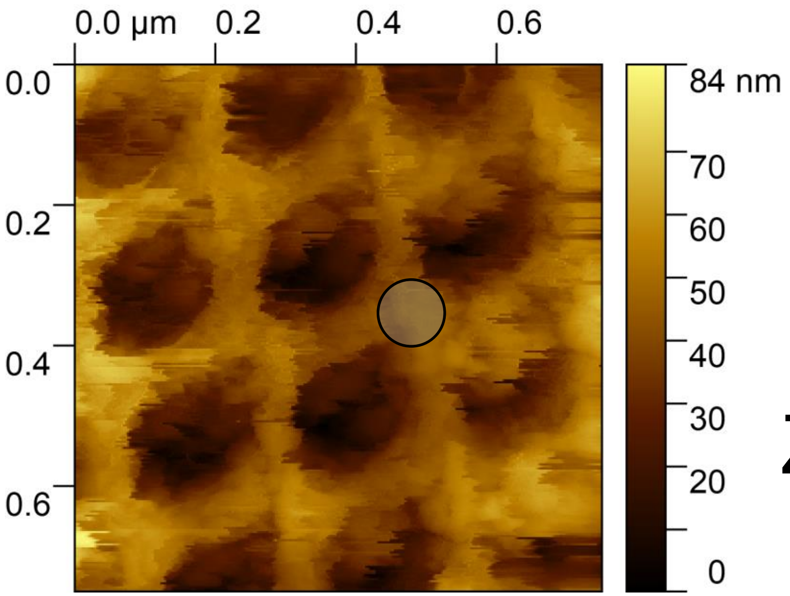


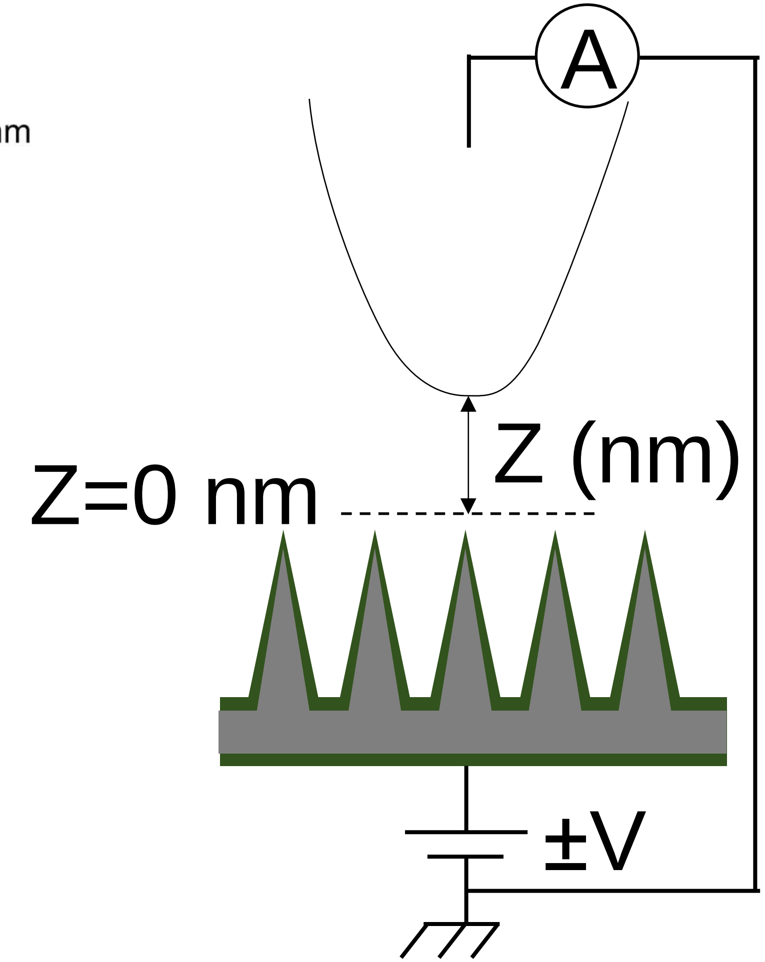


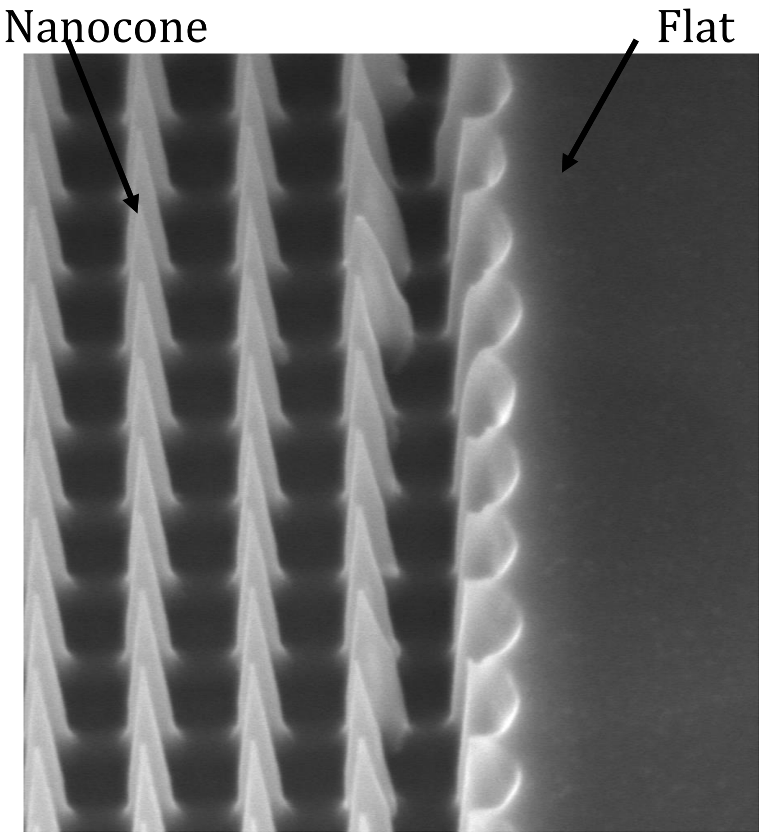
Discrete Z, I(V)-Spectroscopy

Si

PtSi



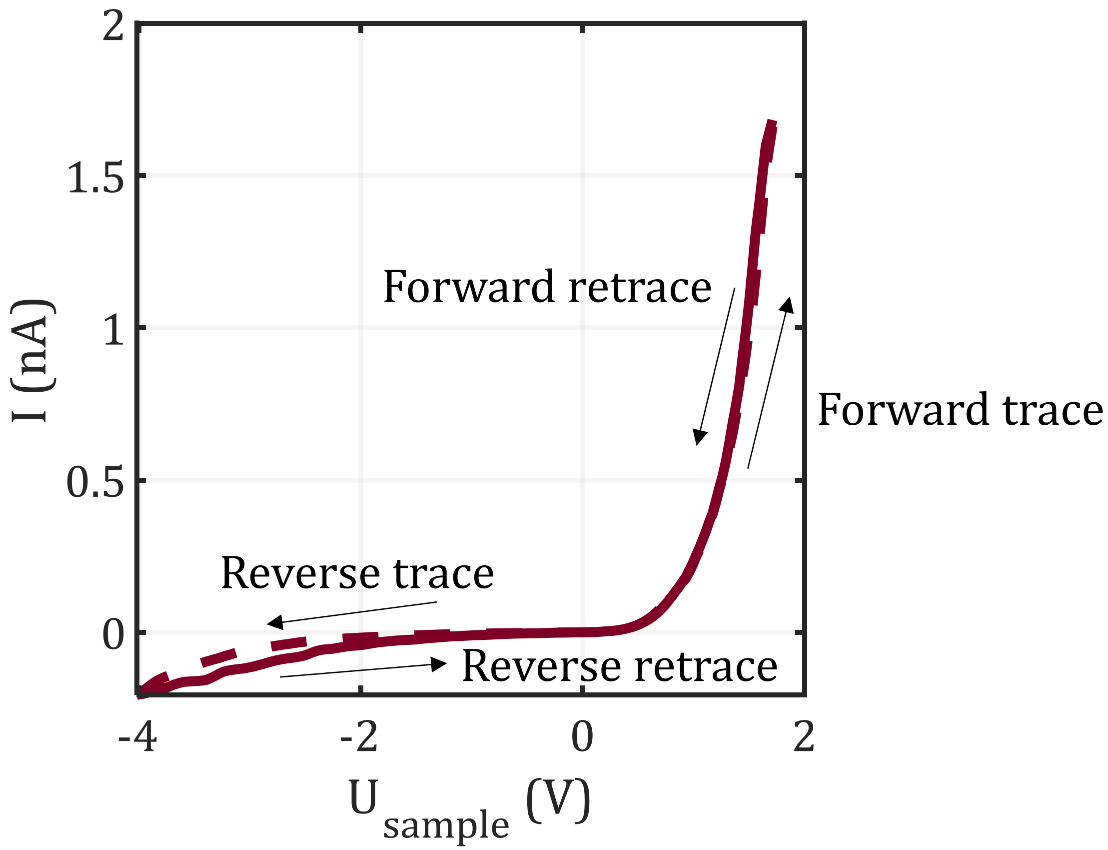




Some background

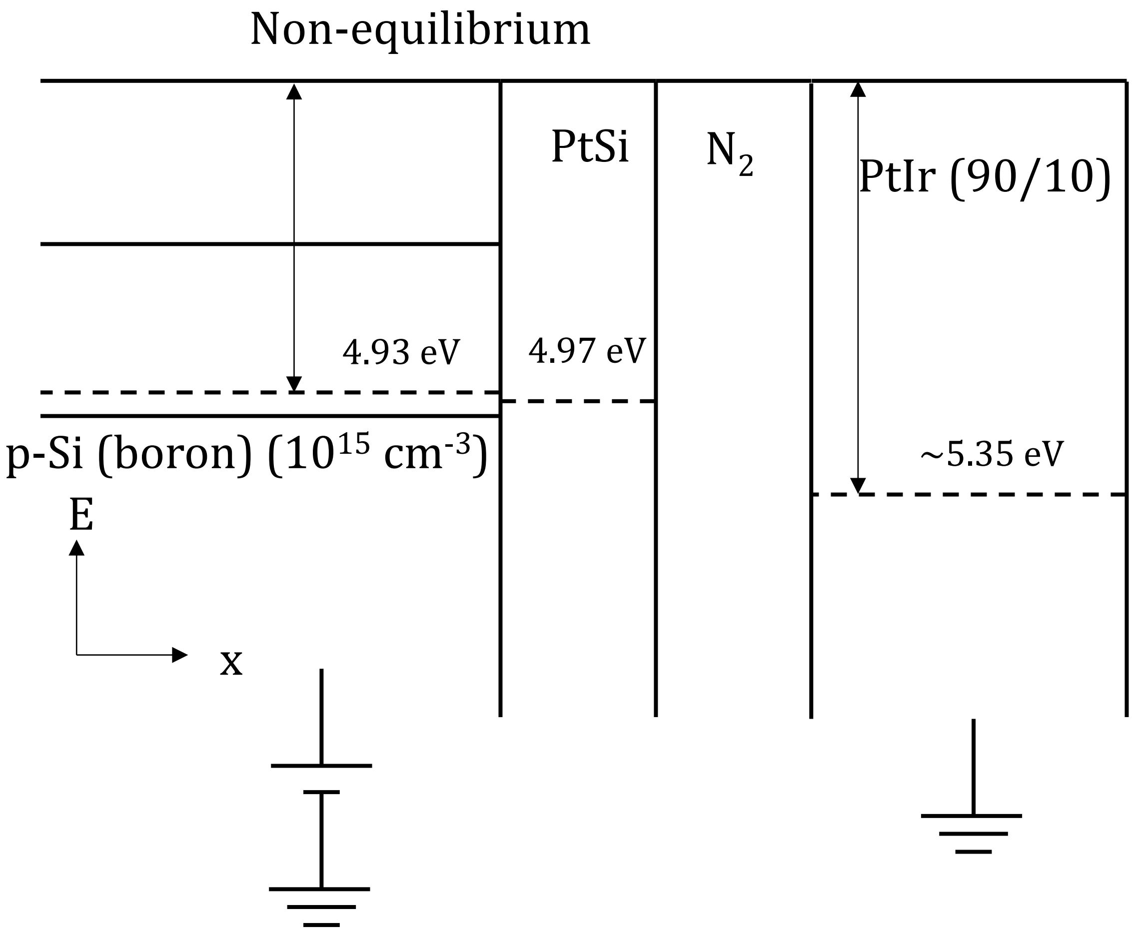
Measurement Conditions

- Approach at ± V_{app} applied to sample (probe grounded)
- Approach current (closed loop) I_{app}= 1 nA
- $Z_{app} \equiv 0$ nm
- Switch off feedback (open loop)
- Record I as function of V_{app}
- V_{set} is either a preset value or a potential at which a limiting current is reached (in the image V_{set} = ±2V or V_{lim} for I_{lim}= 1.8nA)



Band Diagram

- $E_{f,Si} = \chi + E_G - \frac{k_b T}{q_e} * \ln\left(\frac{N_A}{N_V}\right)$
- PtSi (211);(110) (platinum rich ; platinum poor) PtSi formation
- $\Phi_{PtSi} = 4.97\ eV$
- $\Phi_{PtIr} = 5.35\ eV$

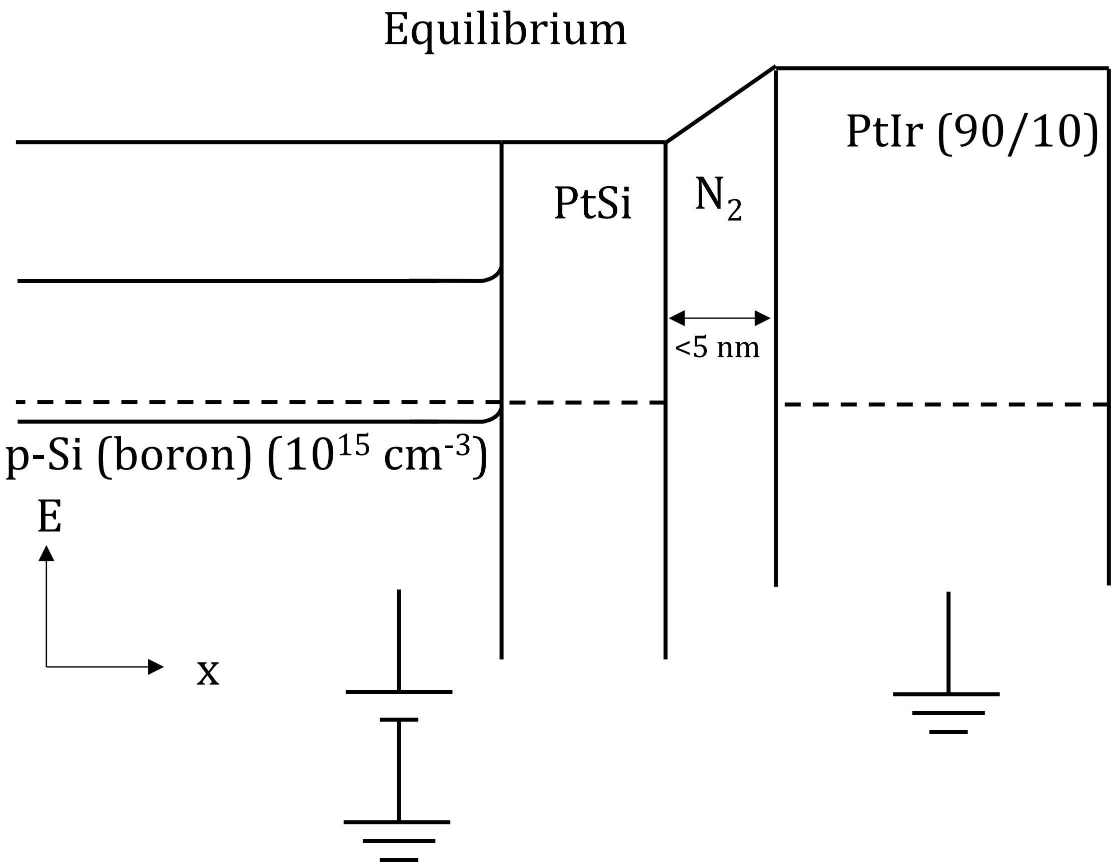


Manish K. Niranjan *et al*. *'Theoretical investigation of PtSi surface energies and work functions'.* Phys. Rev. B. *(2006)*

Band Diagram

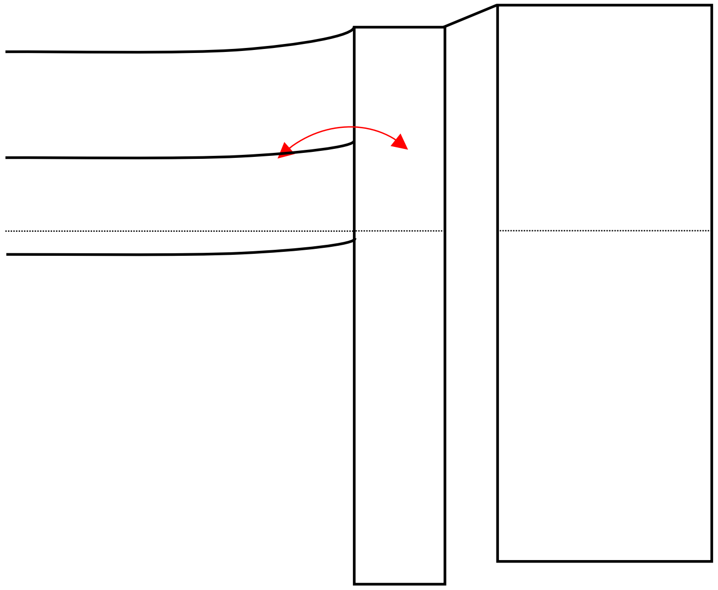
1. $E_{f,Si} = \Phi_{PtSi}$
2. $\Phi_{PtSi} = \Phi_{PtIr}$

The p-type silicon equilibriates with the PtSi, where the metallic PtSi equilibriates with the PtIr probe.



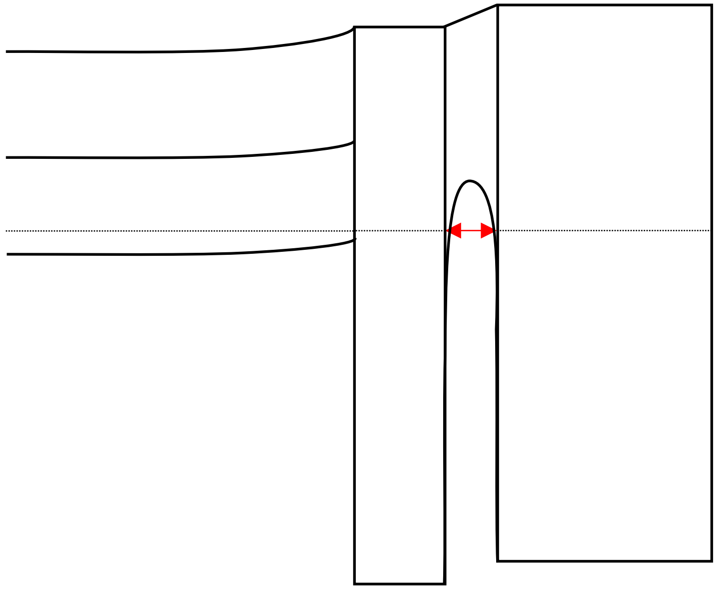
Different Barrier models

Thermionic Emission (TE)



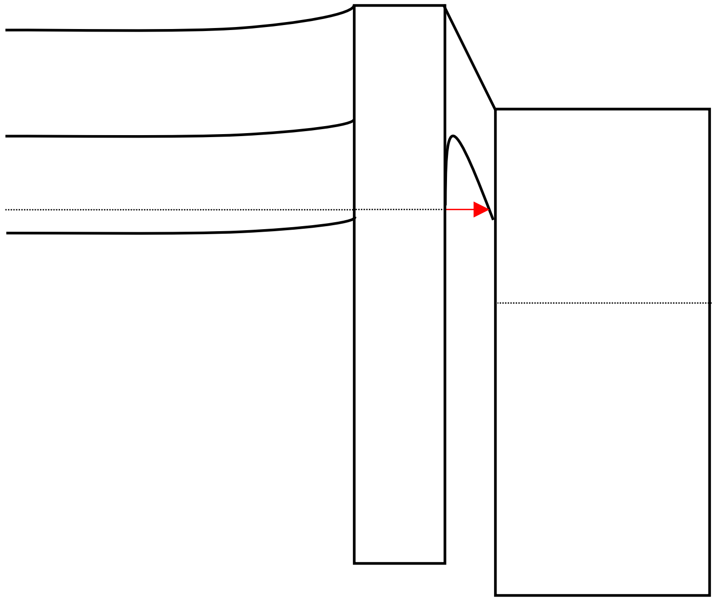
$$\log(I) \propto V$$

Direct Tunneling (DT)



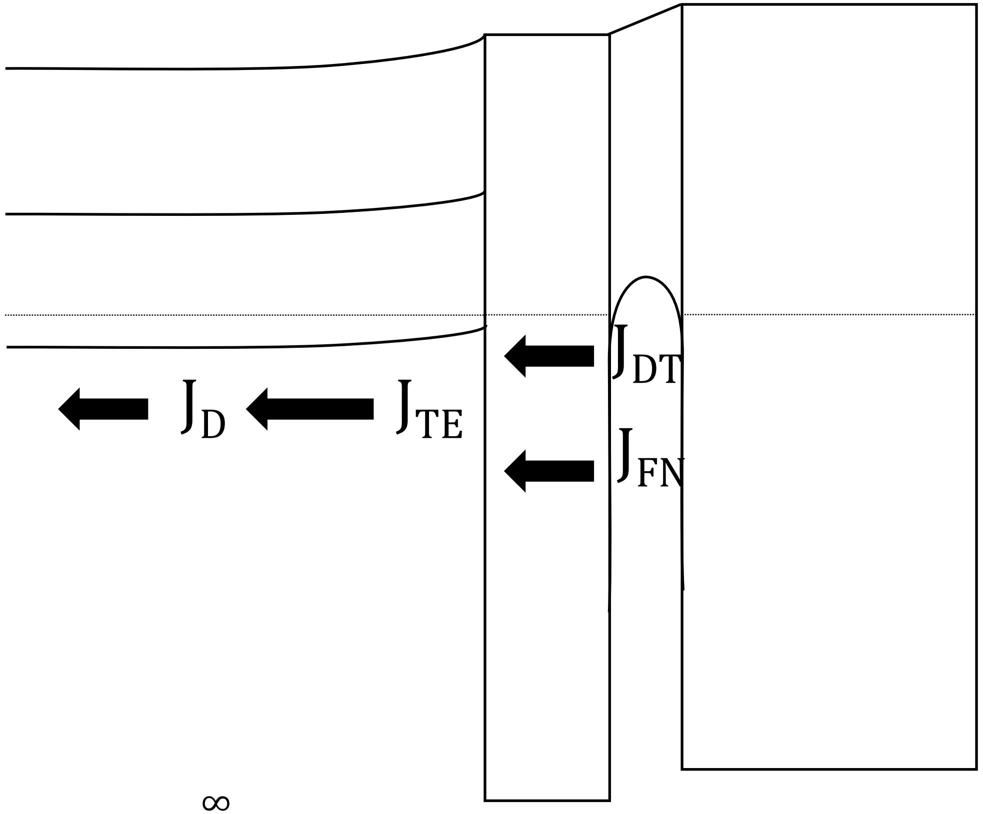
$$\log\left(\frac{I}{V^2}\right) \propto \log(1/V)$$

Field emission (FN)



$$\log\left(\frac{I}{V^2}\right) \propto \frac{1}{\mathrm{V}}$$

Positive potential on Sample

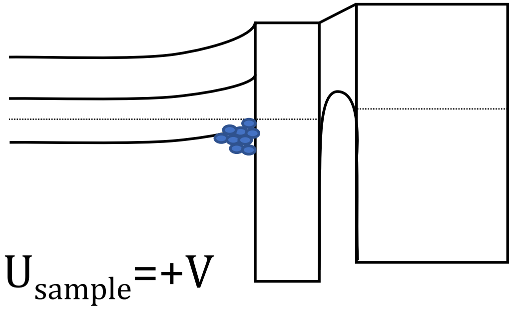


$$J = \int_{-\infty}^{\infty} q.v_x.D(E)dn$$

$$dn = N(E).F(E).dE$$

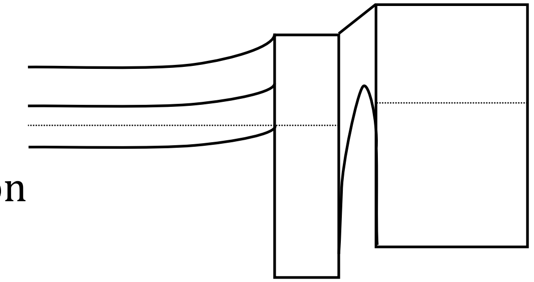
1. $J_{FN} < J_{DT} << J_D$

   Build-up of potential
   In space-charge region.
   Potential at PtSi lowers



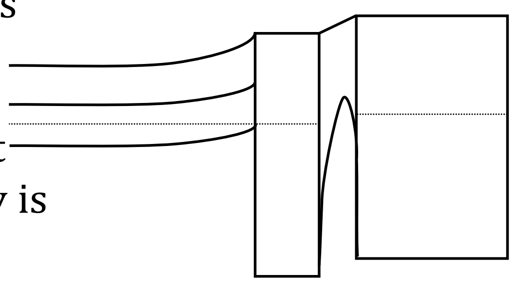
2. $J_{DT} < J_{FN} << J_D$

   Build-up of potential
   In space-charge region
   slowsdown.
   Potential at PtSi lowers



3. $J_{FN} \geq J_D$

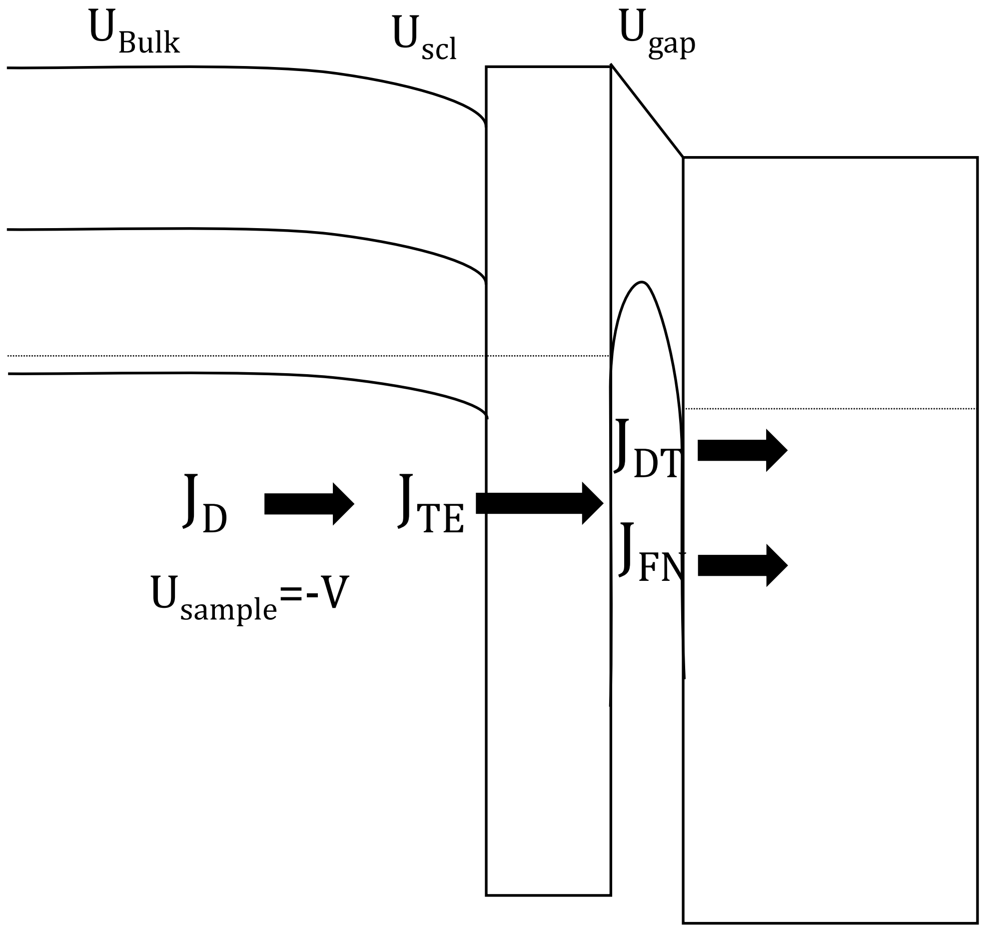
   Barrier is non-existent
   (Tunneling probability is
   Unity). Current is
   controlled by Drift-
   Diffusion.



Negative potential sample

1. $J_{FN} < J_{DT} << J_D$
   Build-up of potential in space-charge region.
   Potential at PtSi increases.

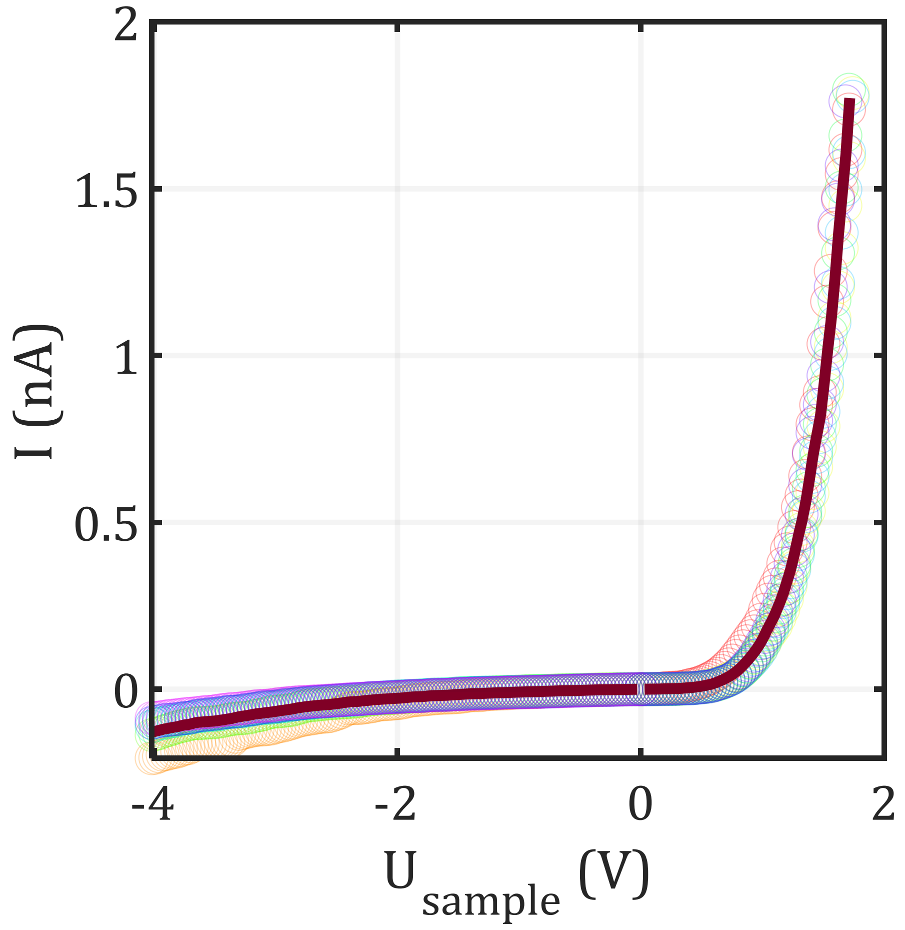
2. $U_{sample} = U_{Bulk} + U_{scl} + U_{gap}$
   Depletion of holes and build-up of elektrons
   At the p-Si PtSi interface (Field penetration)



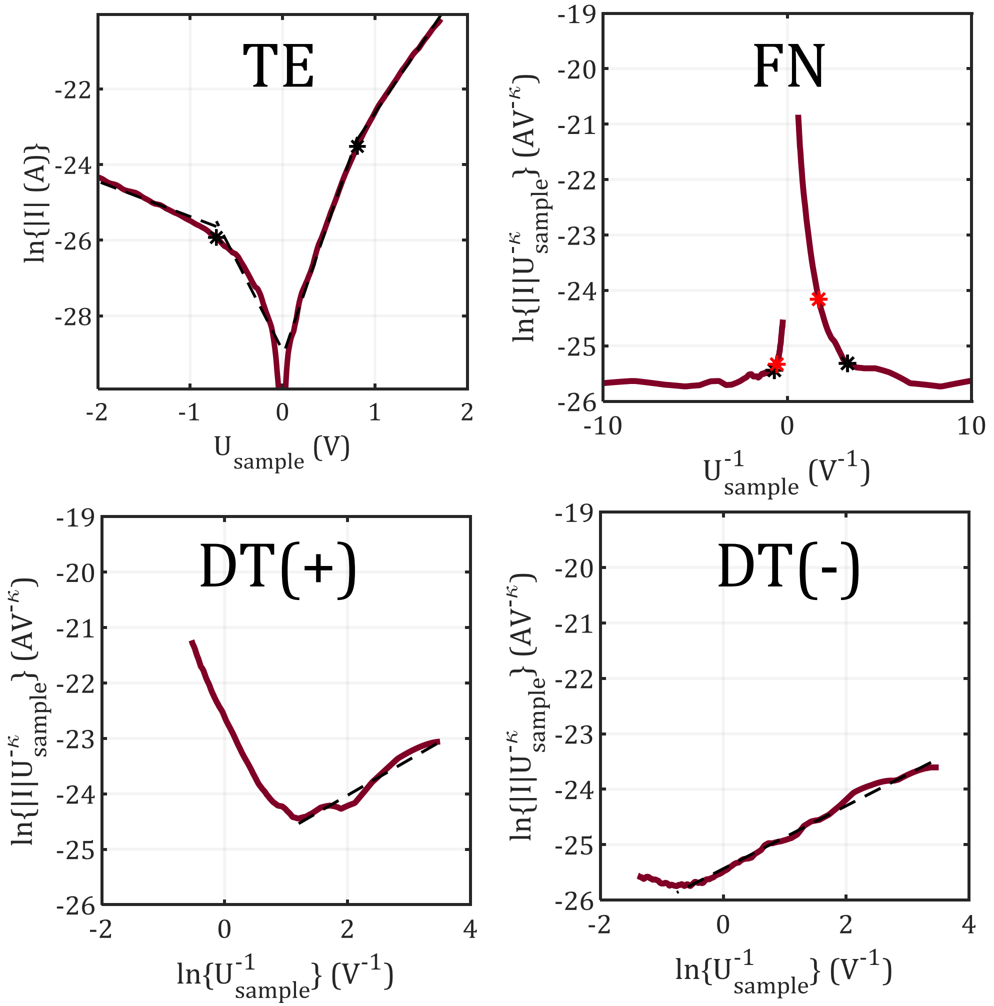
Results

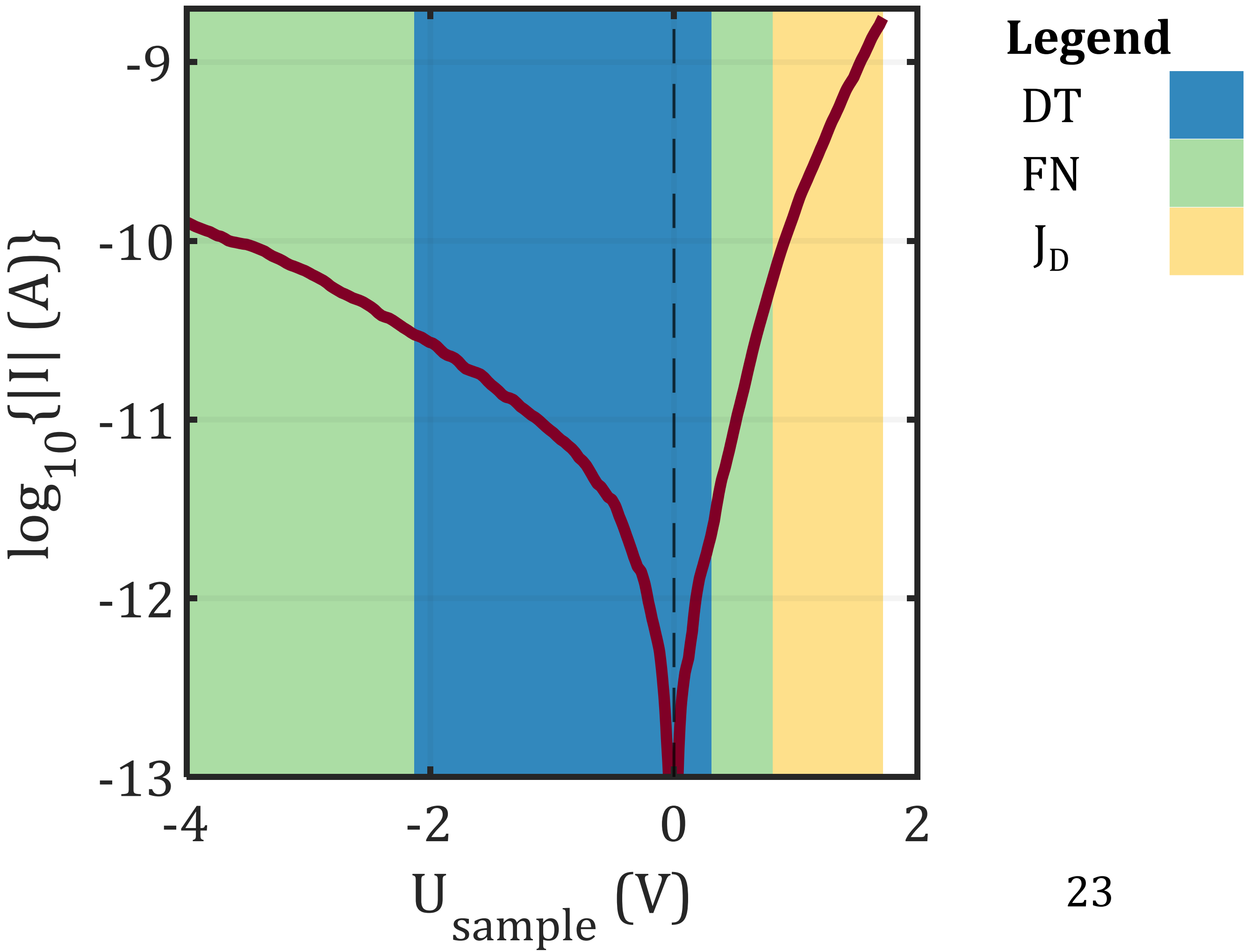
Measurement over flat surface

- Average of 5 measurements over flat surface.
- U_{lim}= ±4 V
- I_{lim}= 1.8 nA



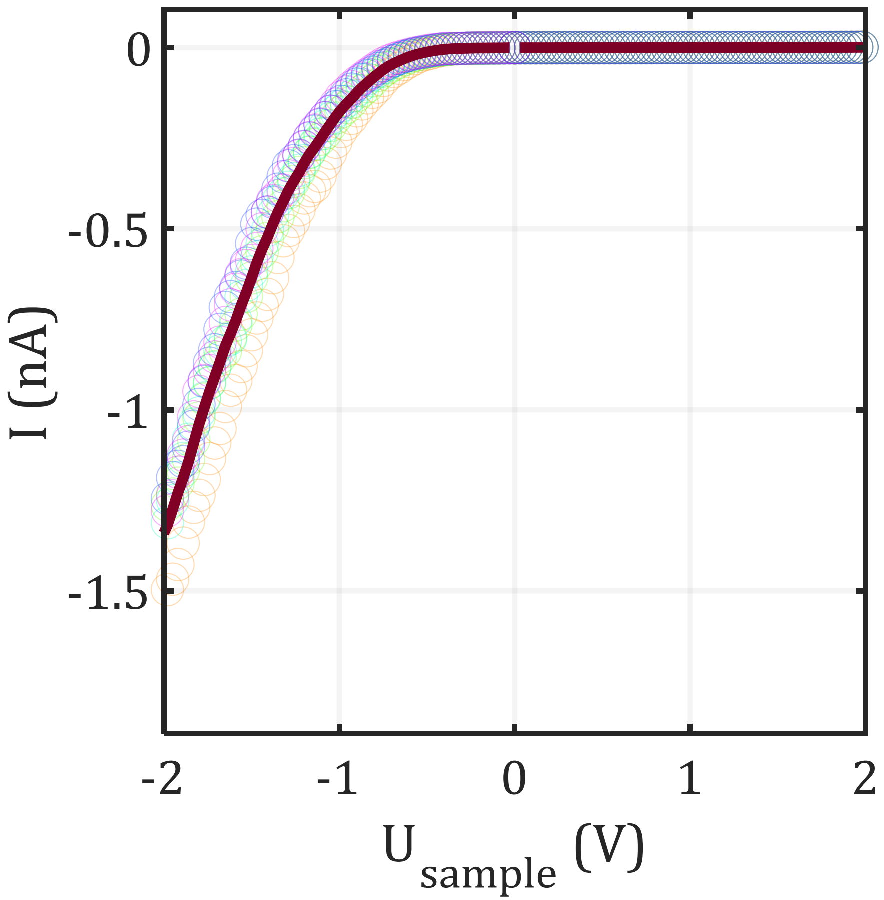
Applying different Barrier models



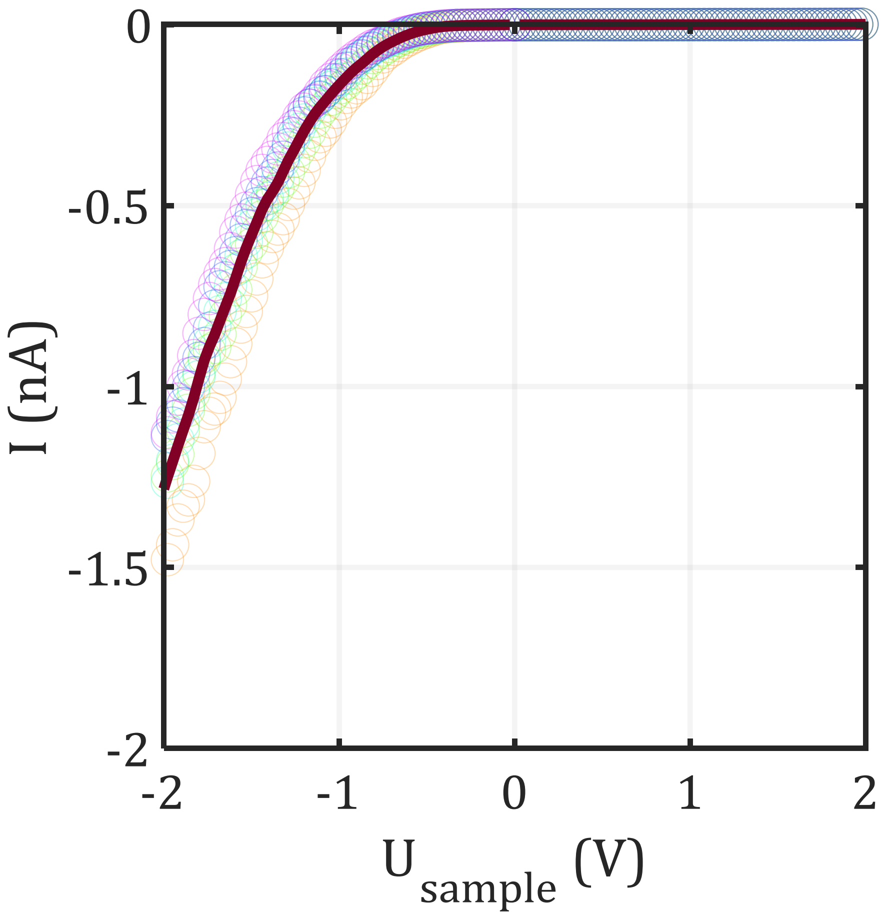


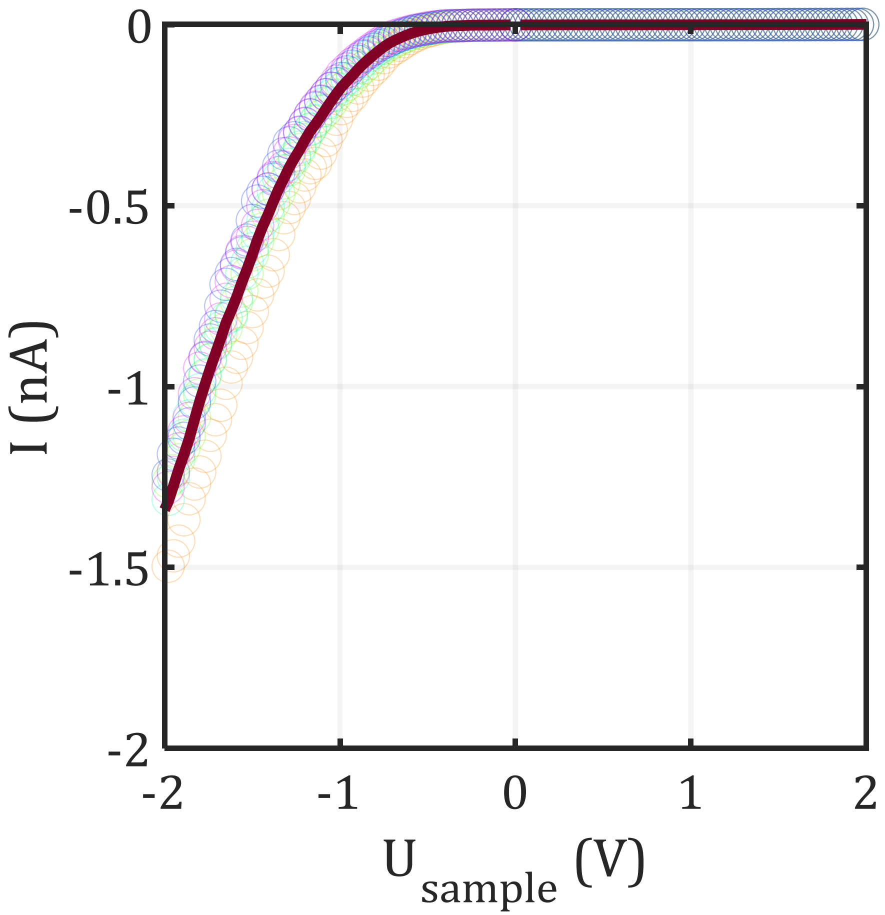
Measurement over Cone

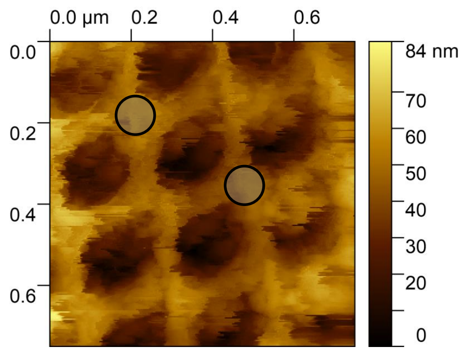
- Average of 5 measurements over conical surface.
- U_{lim}= ±2 V
- I_{lim}= 1.8 nA



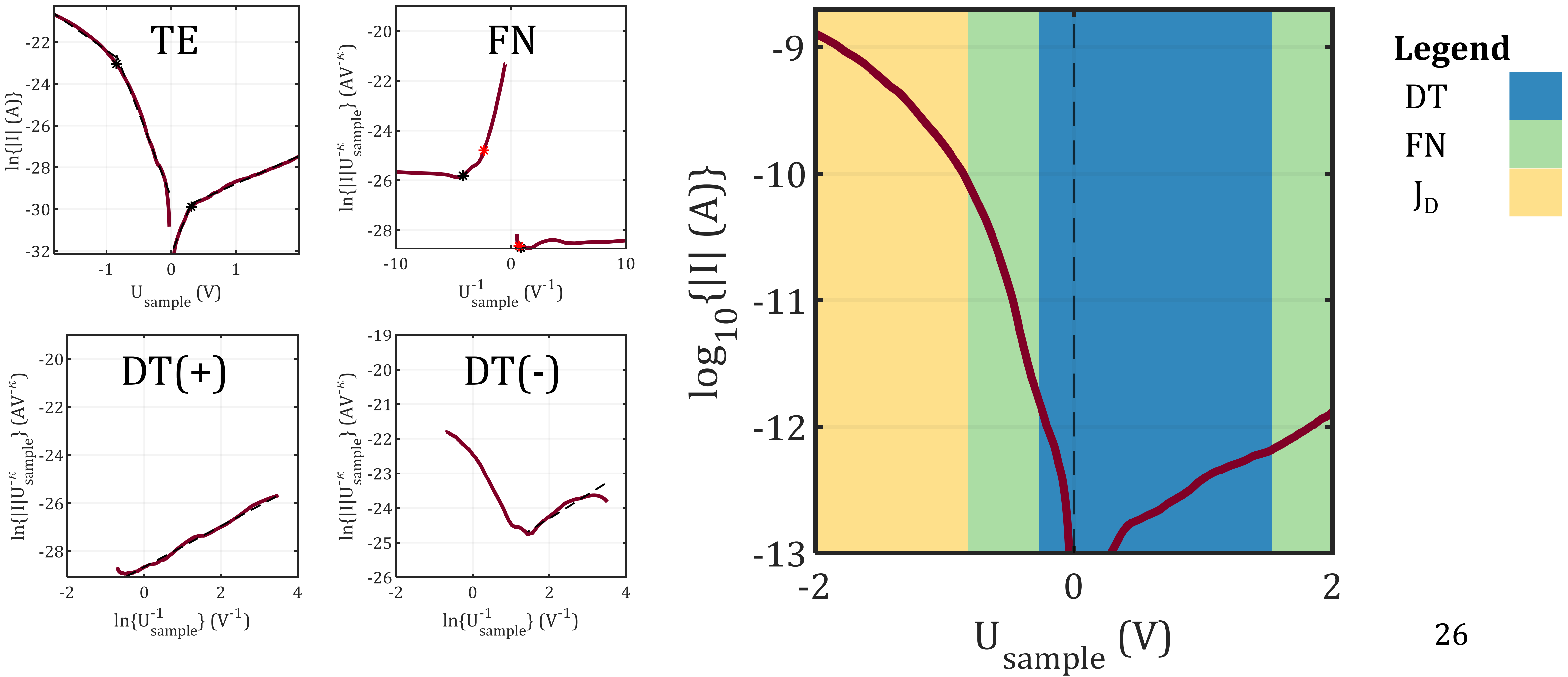
Measurement over two different cones



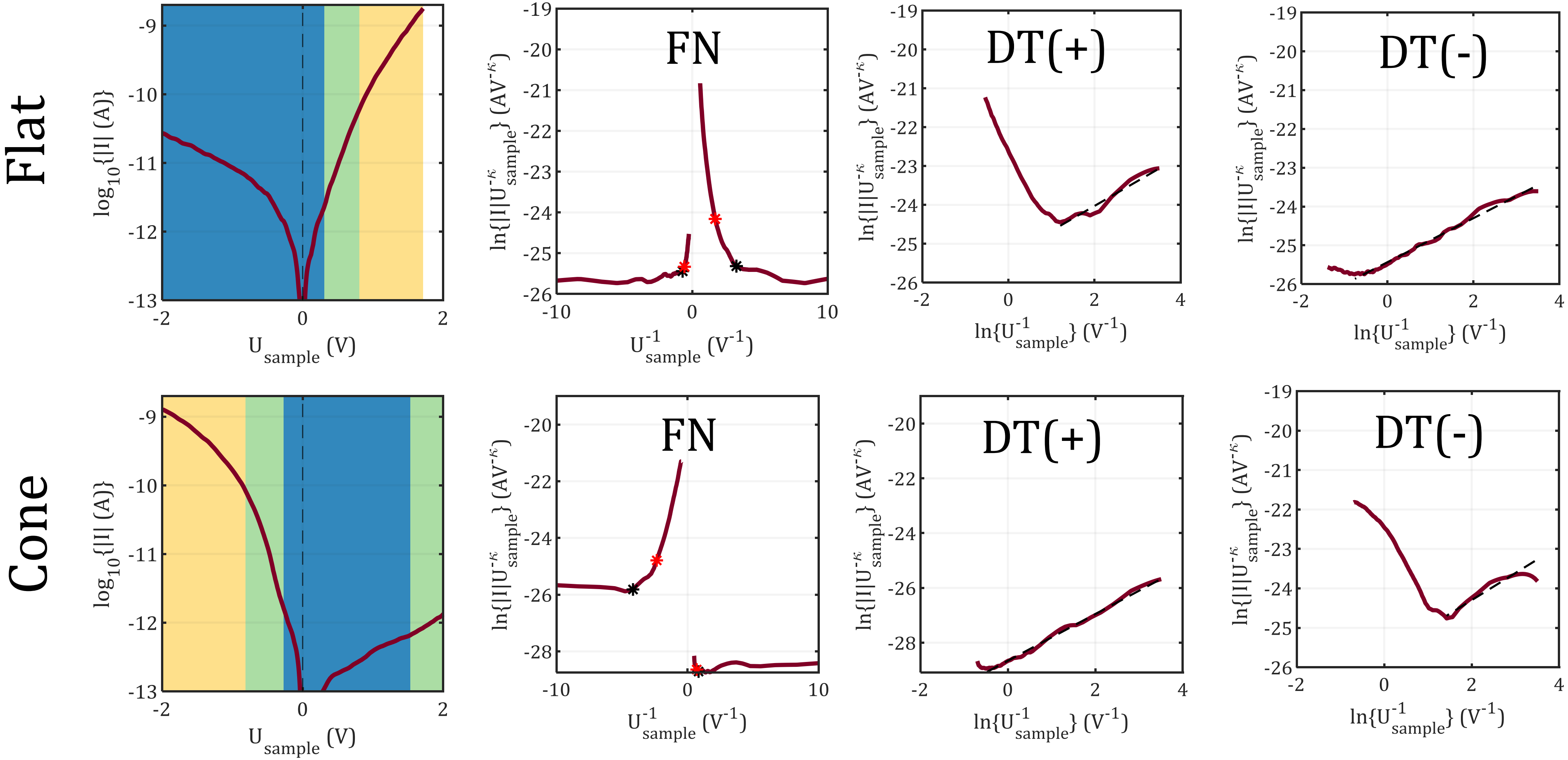




Again: Applying different Barrier models

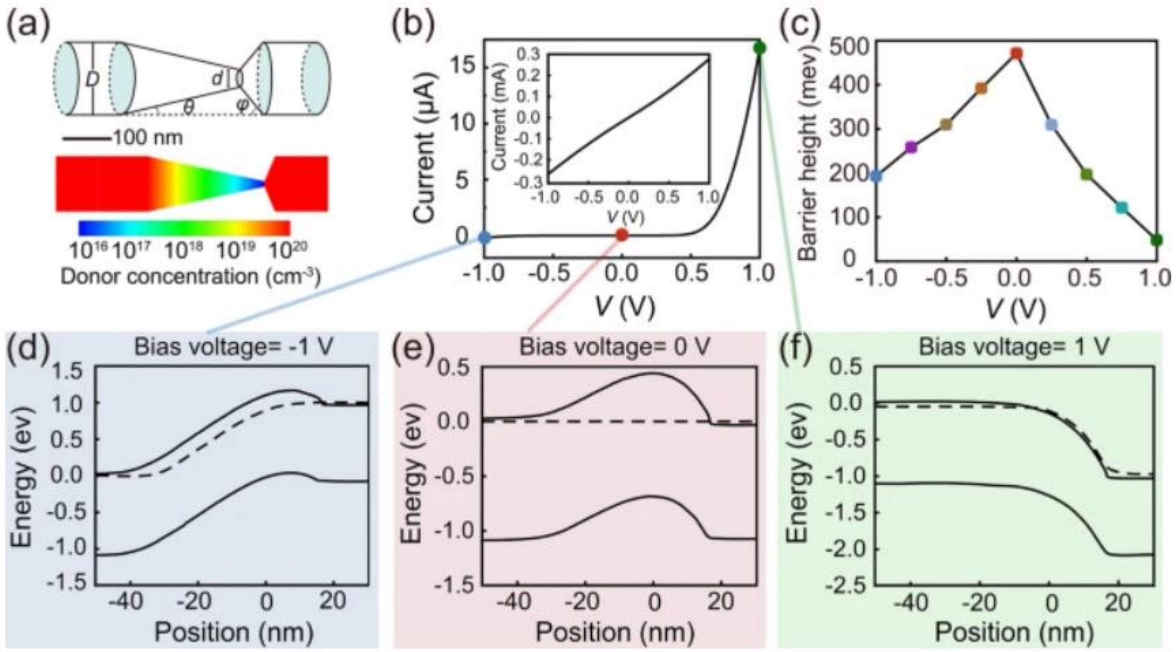


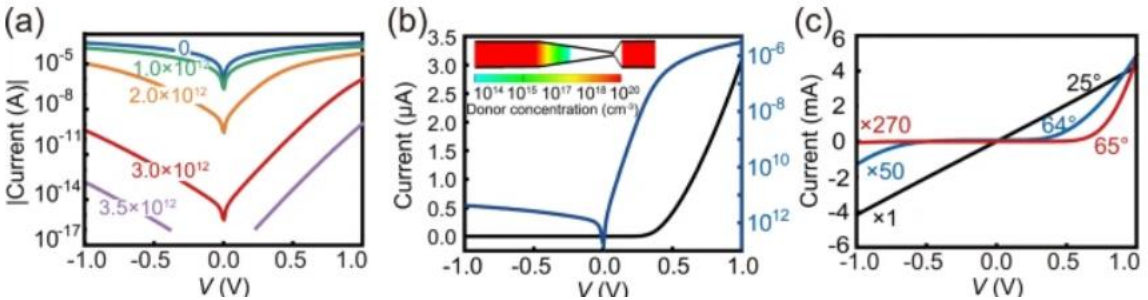
Comparison of flat and cone



A Geometric diode

- Key factors:
  - surface states
  - Geometry
  - surface passivation

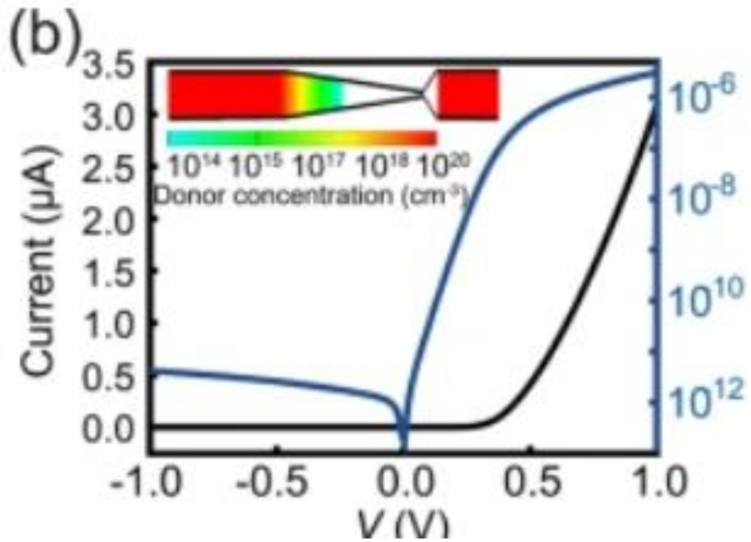


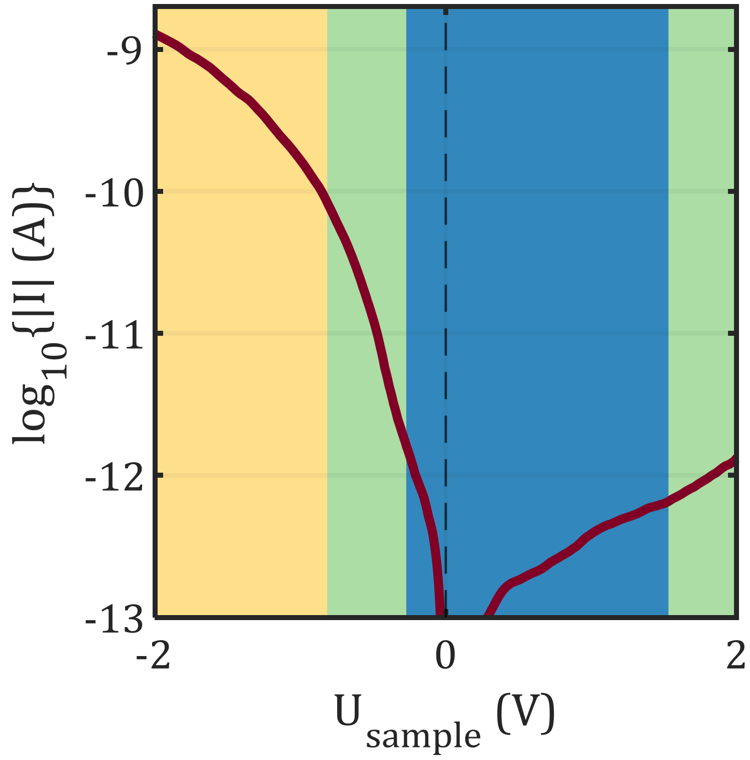


M. Bai*et al.* *'Asymmetric bias-induced barrier lowering as an alternative origin of current rectification in geometric diodes'.* Nat. Com.PhysB. *(2021)*

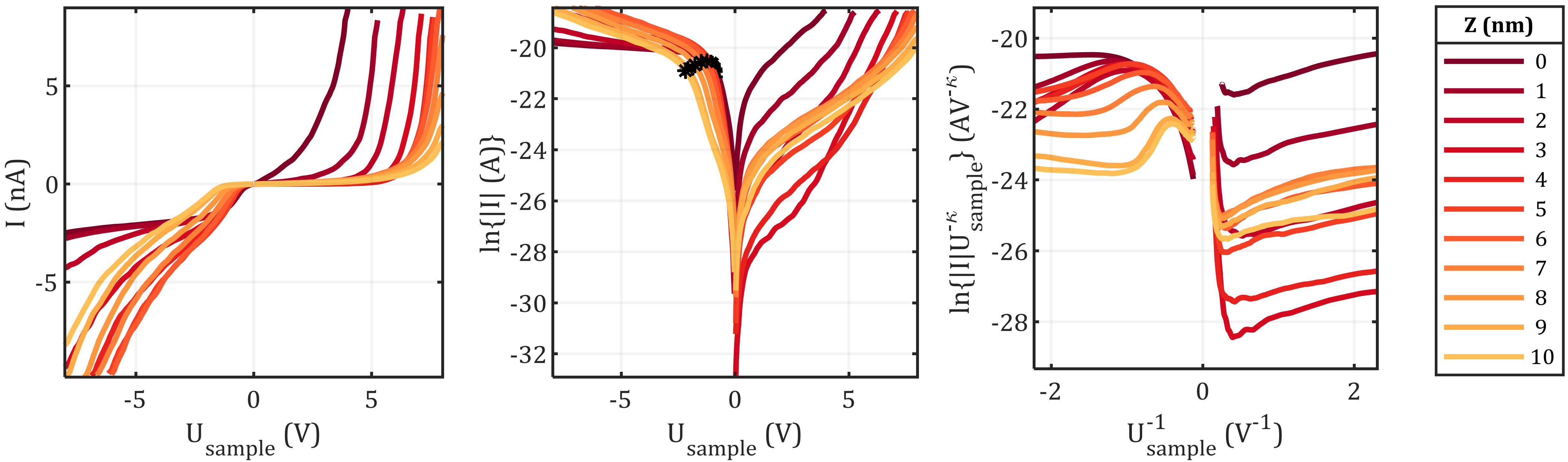
Summarizing

- PtSi coated p-Si nanocone arrays are inherently transport limited devices
- Effect of PtSi is yielding an n-type current voltage behavior possibly due to surface states, and pinning effects.



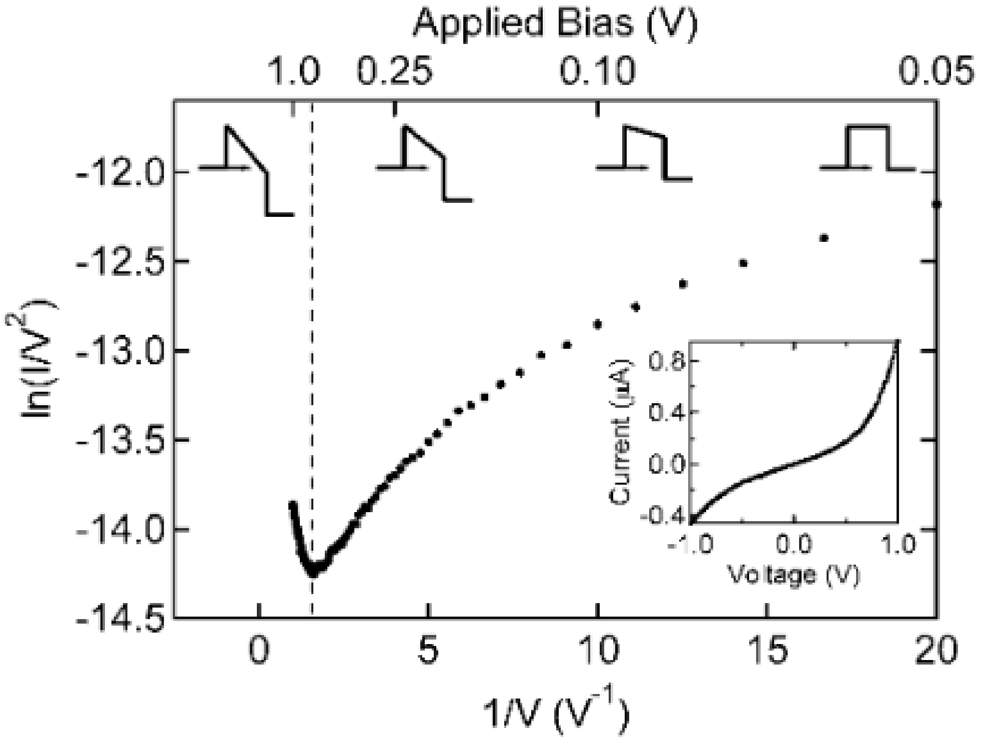


Moving away from the substrate



The transition Voltage

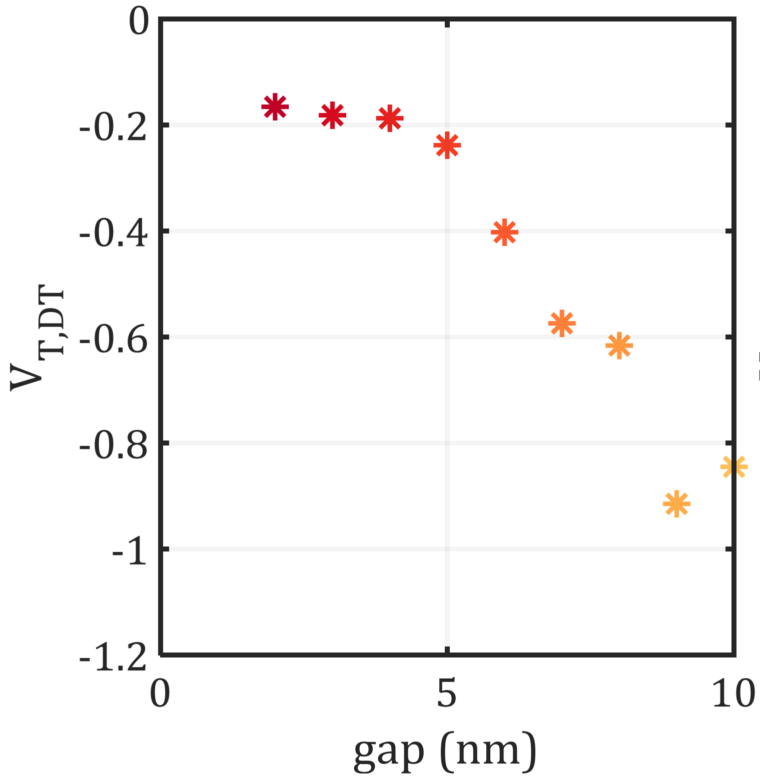
- Transition Voltage determines the Crossover point from DT to FN regime
- Furthermore, we can consider the knee voltage at which the Current is substrate limited

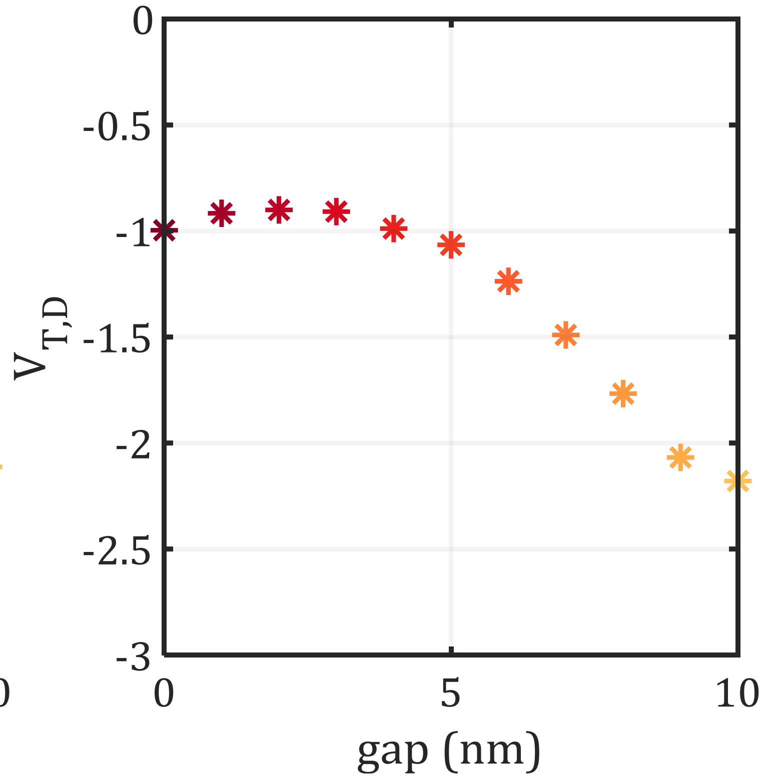


Jeremy M. Beebe *et al*. *'Transition from Direct Tunneling to Field Emission in Metal-Molecule-Metal Junctions'.* Phys. Rev. Lett. *(2006)*

Transition voltage

- Since the increase in gap is 10 nm, why $V_{T,DT}$ only moves by 1V or so
- Remarkable correlation between DT-FN regime change and Substrate limited current.
- Field emission eventually becomes substrate limited

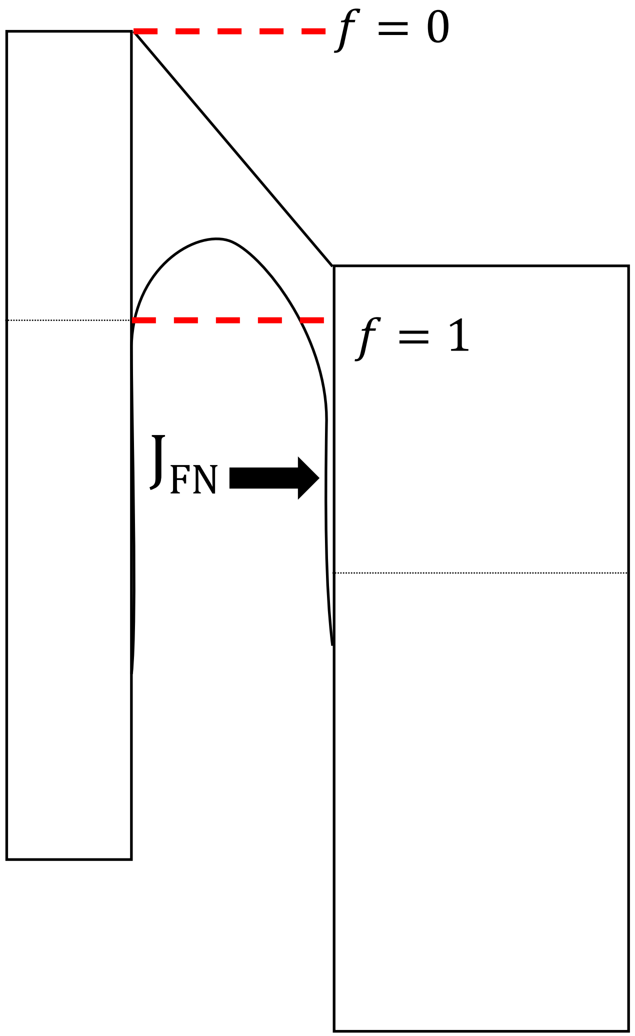


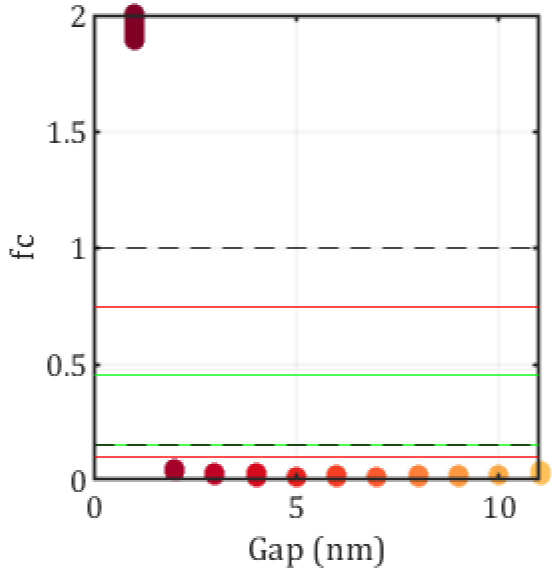


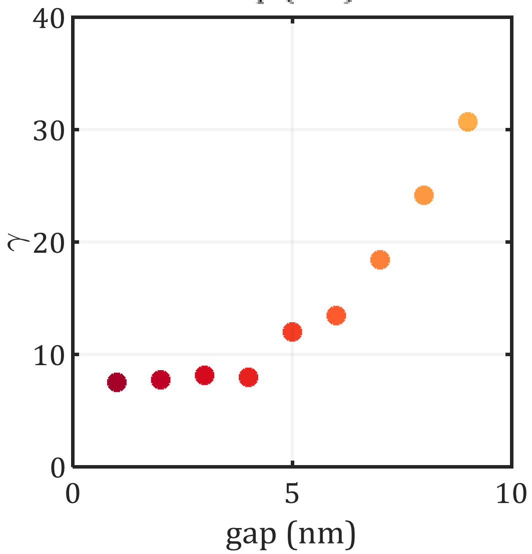
How to explain

- $J = \int_{E_c}^{\infty} q.v_x.D(E)dn$
- $dn = N(E).F(E).dE$
- What about the barrier transparency (E-Field)

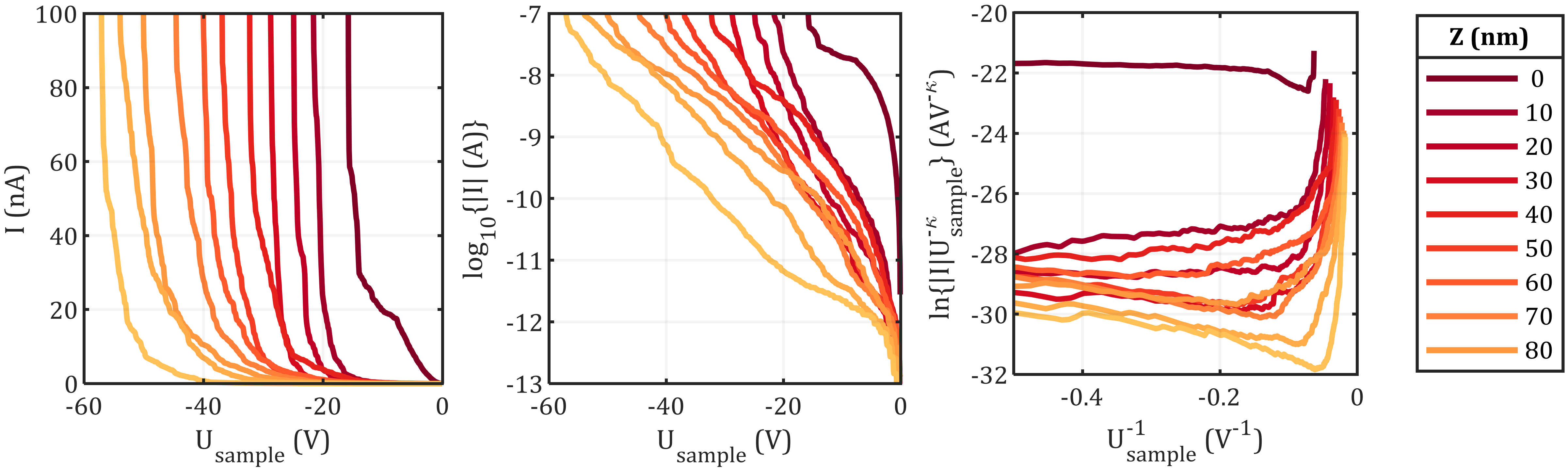
- $f = \frac{F_L}{F_R}$
- $\gamma = \frac{gap}{\zeta_{ex}}$
- $\zeta_{ex} = \frac{S_{fit,MG}}{b_{FN}.\Phi_{PtSi}^{\frac{3}{2}}}$







Even larger gaps



Same argument holds: Tunneling Barrier vs. Substrate limited current → Relate to mr. Edler

Large gap measurements

nto hexane under ambient
on emission from SiNW's.,"
eactions, 2016
of silicon nano-pillar arrays
echnology (2020)
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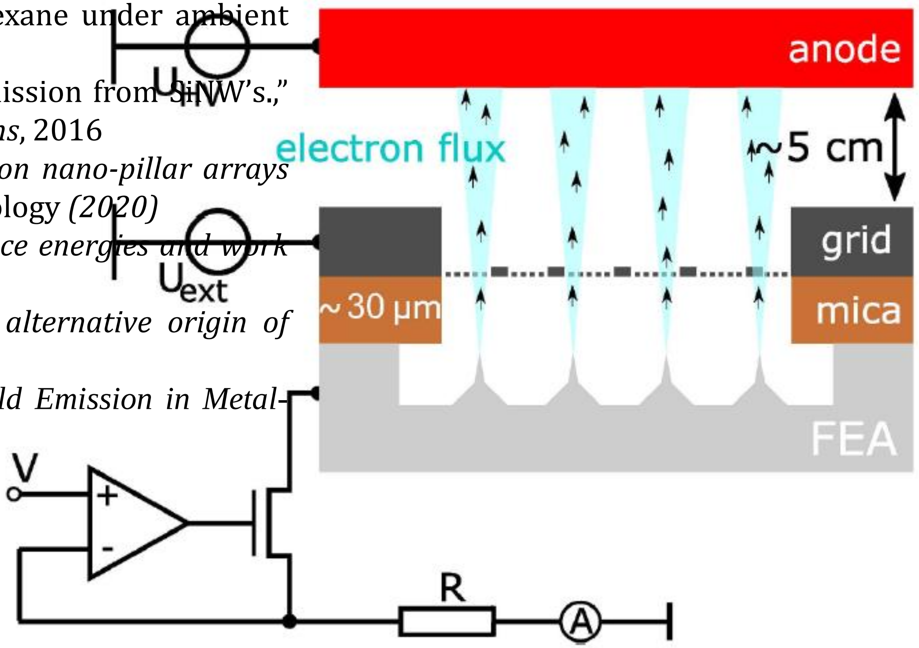
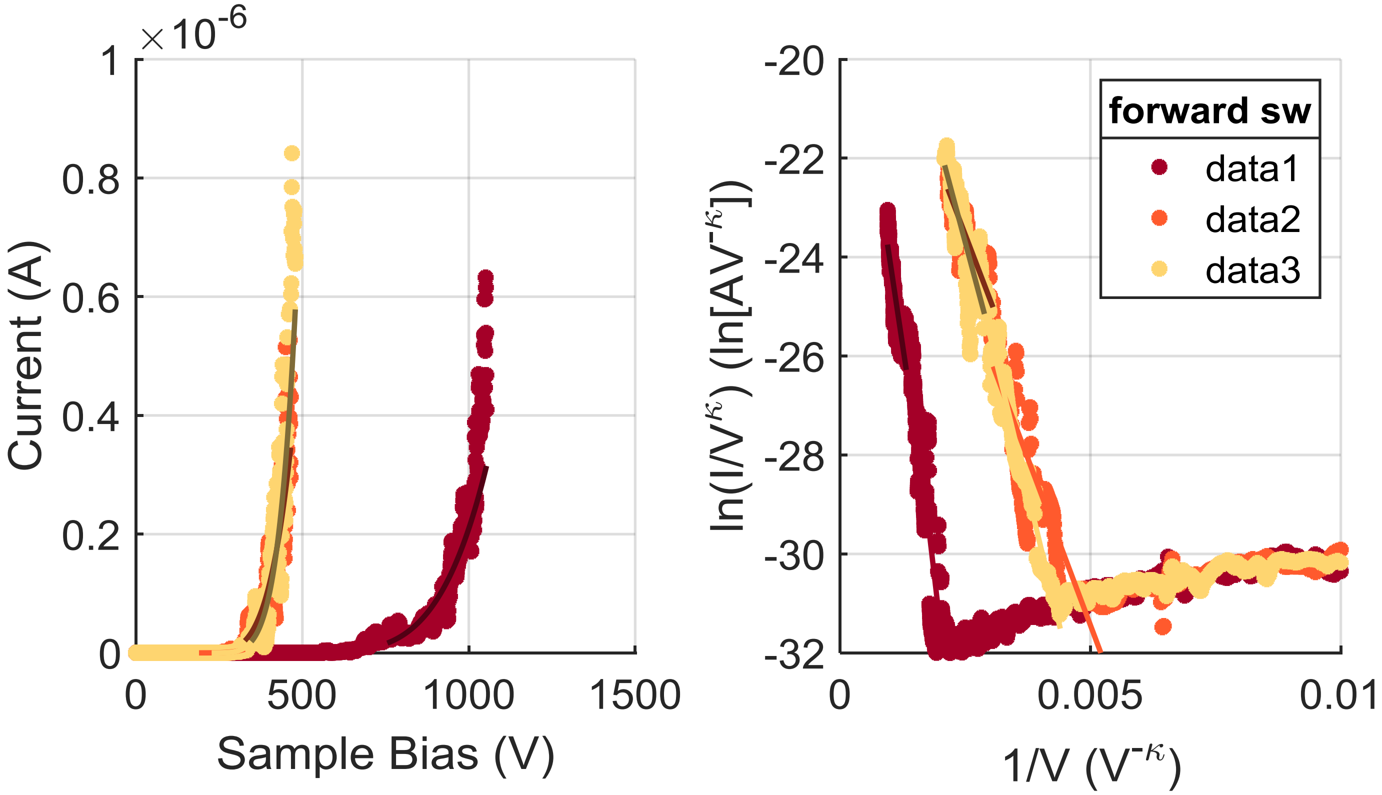
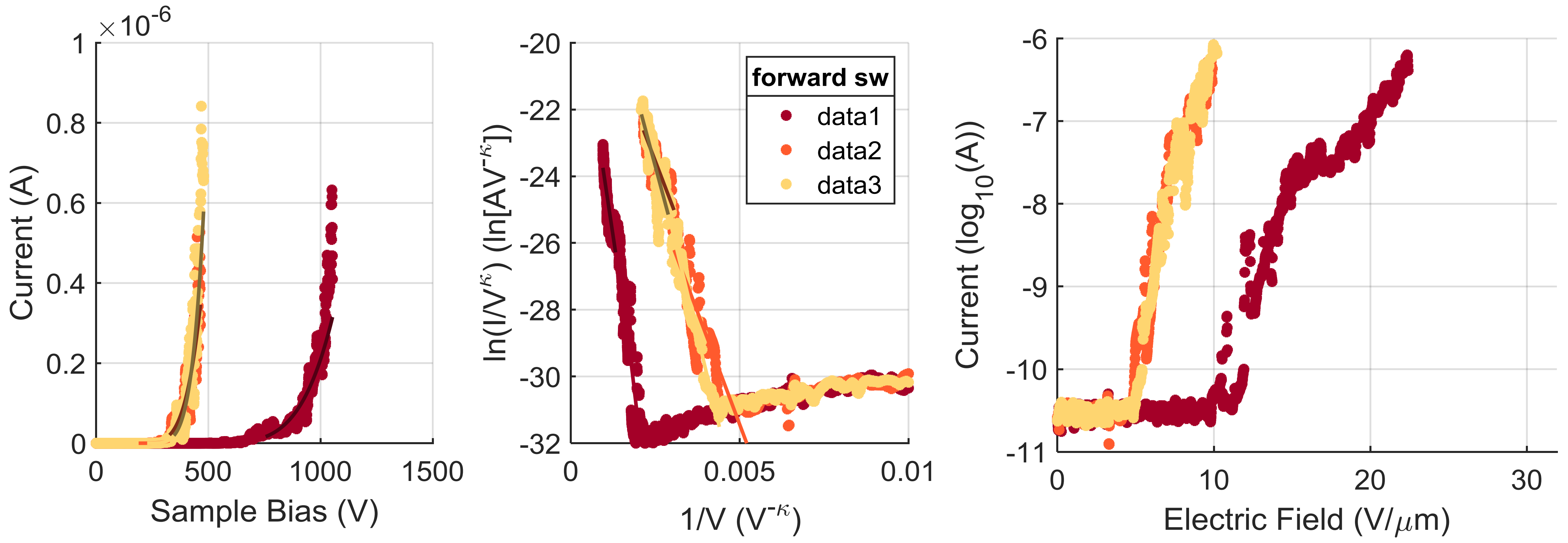
2021)
to Field Emission in Metal-
and



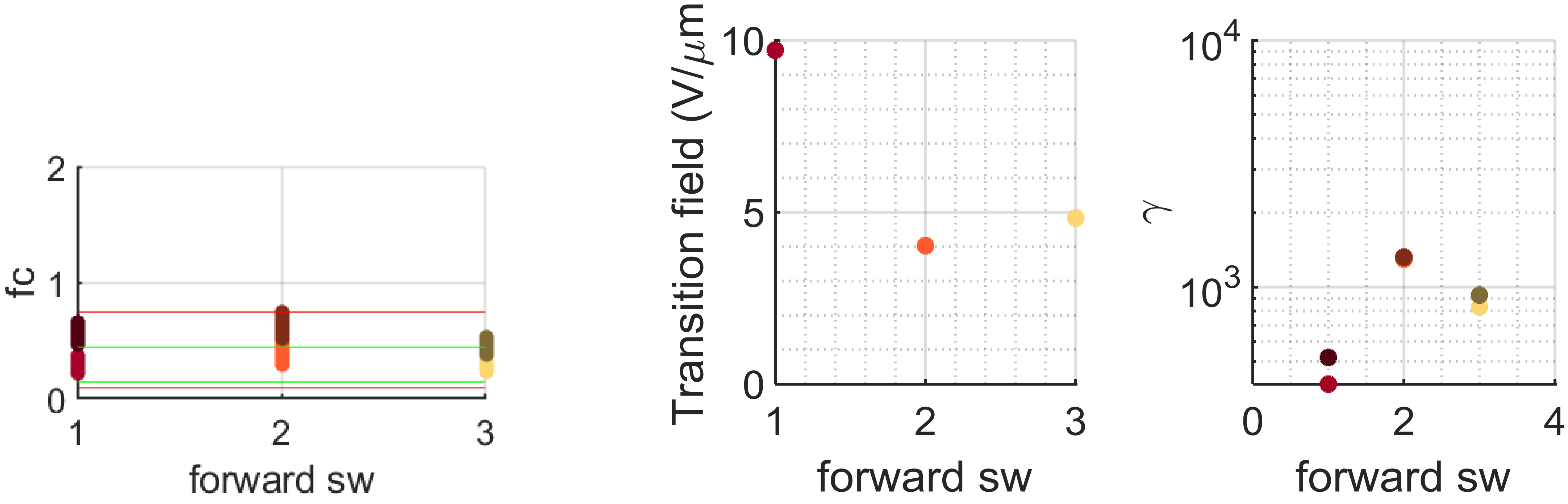


S, Edler *et al*. *'Silicon field emitters fabricated by dicing-saw and wet-chemical-etching '*. J. Vac. Sci. Technol. B*(2021)*

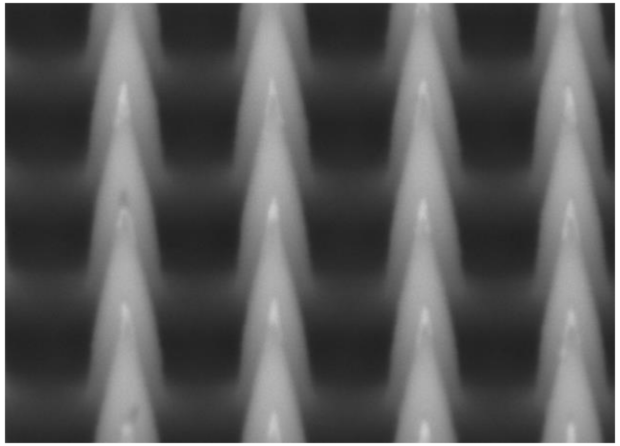
Barrier models



Field emission properties



Conclusion



- Presented a way to obtain highly homogeneous silicon field emitter array
- Possibility to (locally) silicidize the array.
- Used STM measurements to show the transition from barrier limited to transport limited behavior
- Verified Field emitter performance in large gap system

D. Jonker

Mesoscale chemical systems (MCS)/

Physics of Interfaces and Nanomaterials (PIN)

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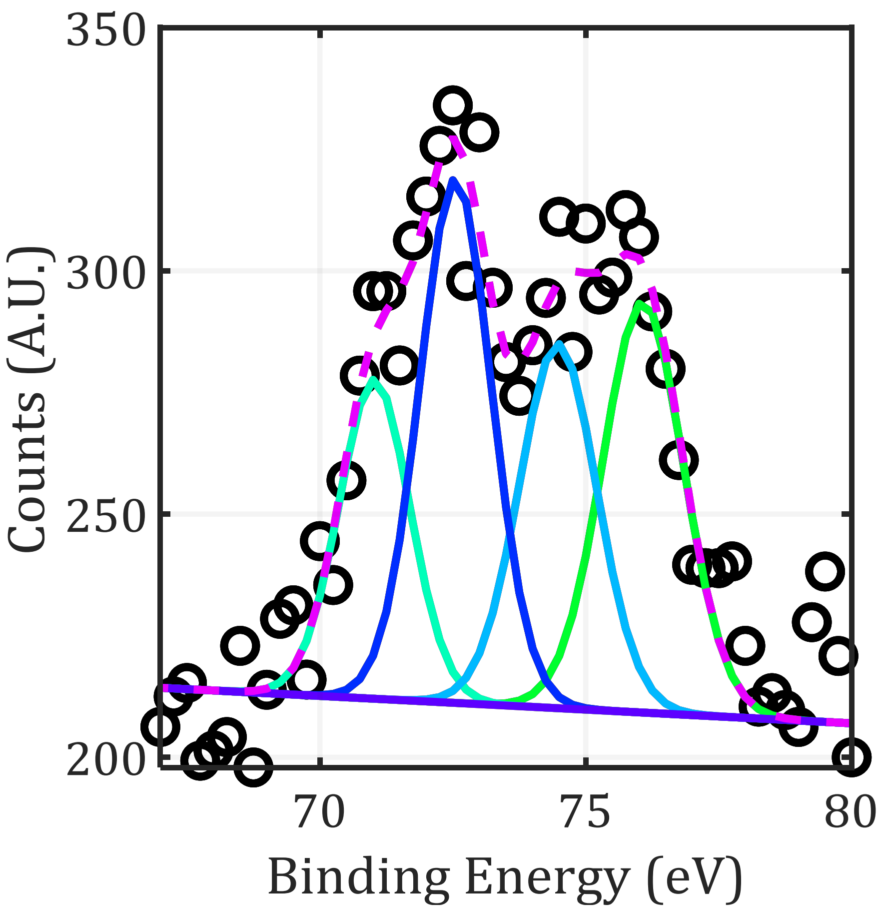
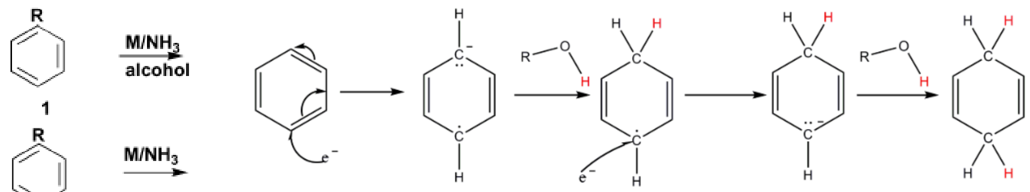
XPS data on PtSi

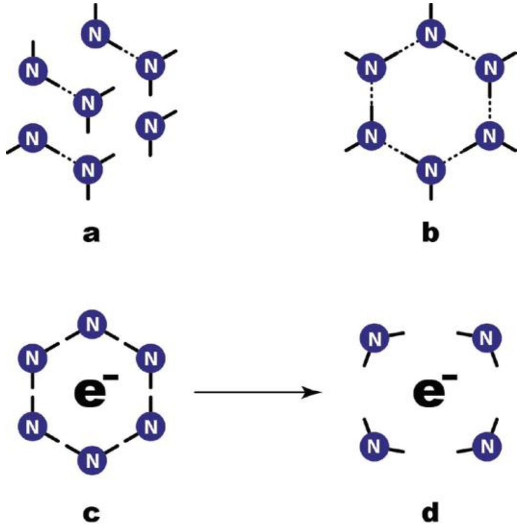
	$Pt4f_{5/2}$		Pt_xSi_{1-x}	$Pt4f_{7/2}$
Position	76.1	71.0	74.5	72.5
FWHM	1.8	1.6	1.7	1.6
Area	163	111	139	185
Lineshape	GL(20)	GL(20)	GL(20)	GL(20)



The solvated electron

Classic Birch Reduction





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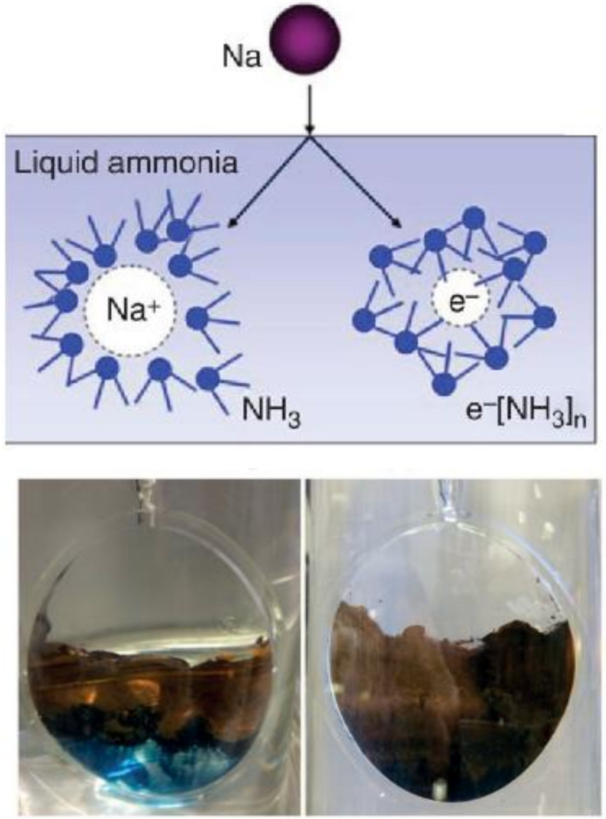

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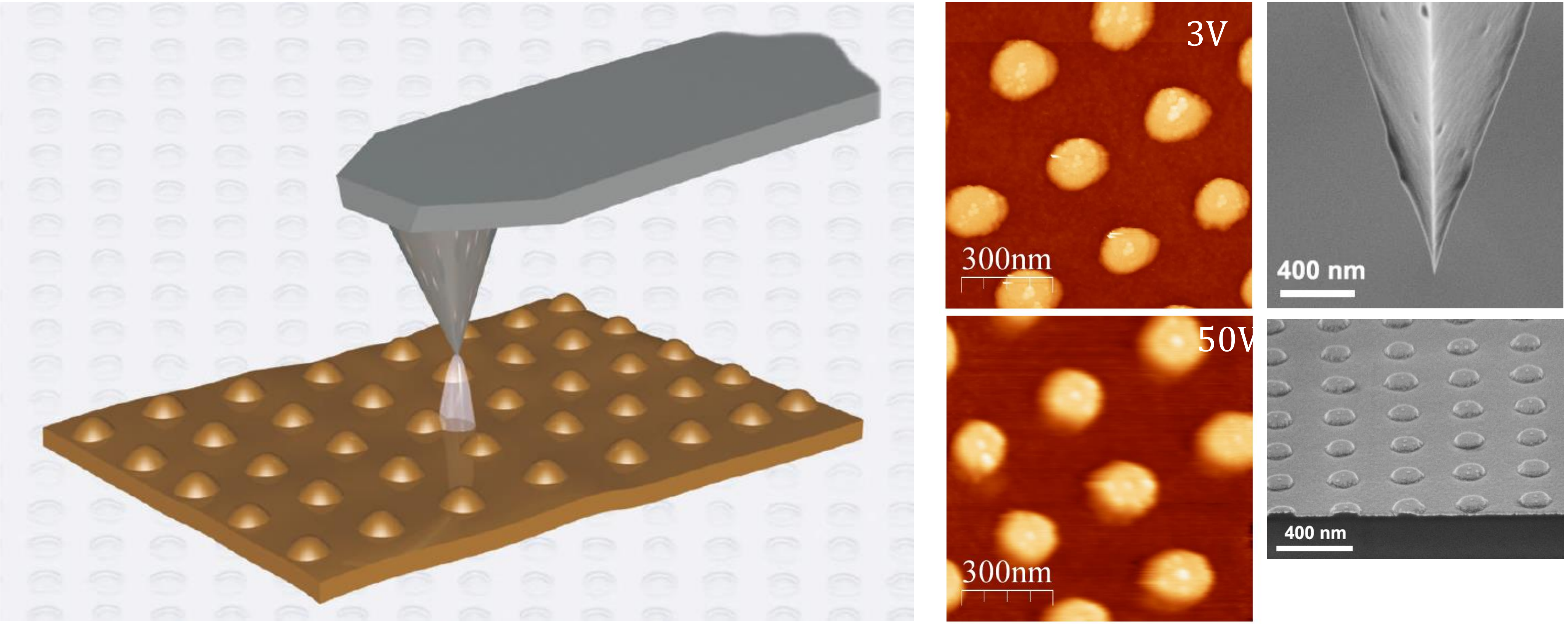
Scanning tunneling microscope (AFM)



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Moving towards the substrate