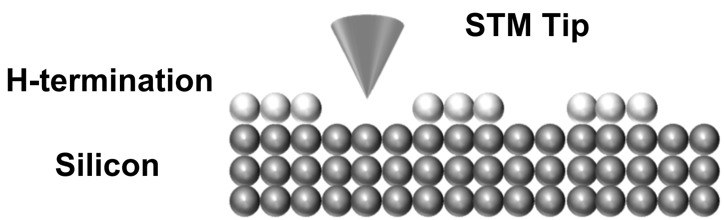

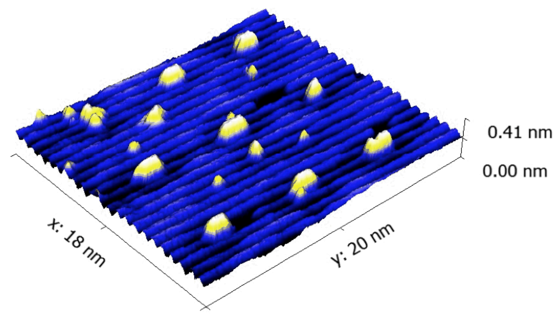

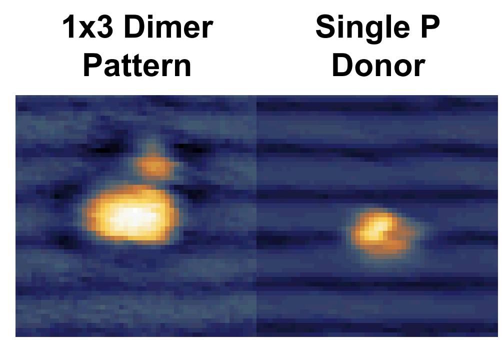

Atomically Precise Single Donor Placement by STM Lithography

J. Koepke (jkoepke@sandia.gov), D. Scrymgeour, R.J. Simonson, M. Marshall, D. Ward, R. Muller, P. Schultz, A. Baczewski, M. S. Carroll, S. Misra, E. Bussmann

Sandia National Labs, Albuquerque, New Mexico, USA

2016 CINT User Meeting

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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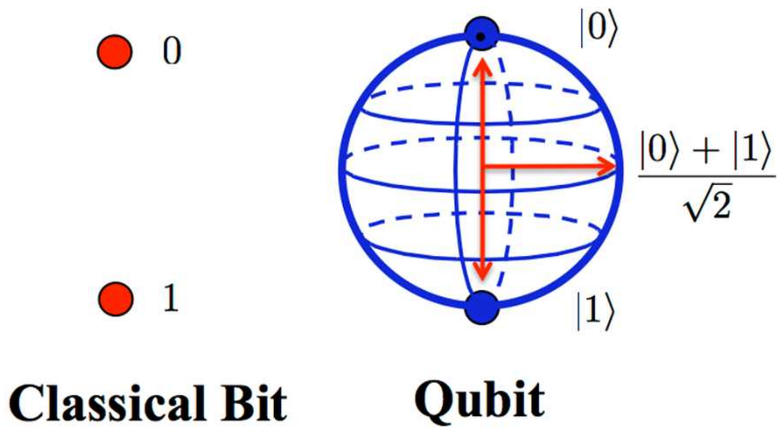
Overview/Motivation

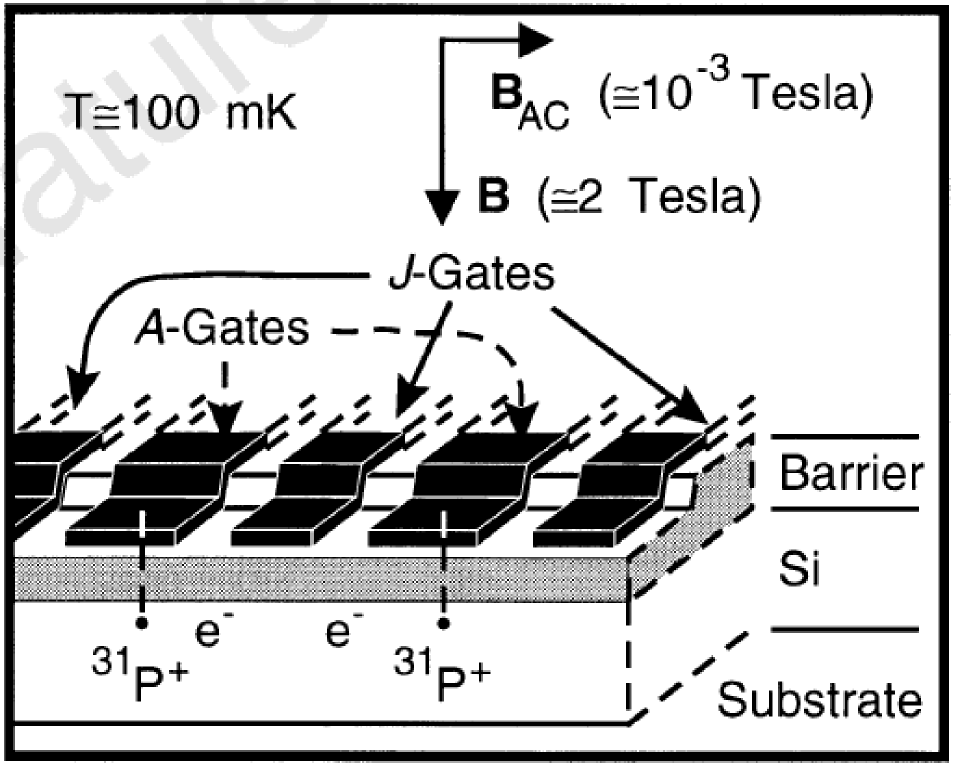
- Motivation for Single P Donors in Si
- Donor Placement by STM Hydrogen Lithography
- Limitations to Donor Placement Yield
- Lithographic Arrays – Improving Target Pattern Yield
- Chemistry of P Donor Incorporation – Comparison of Experiment with Simulations

Single Donors in Si for Quantum Bits



Classical Bit vs. Quantum Bit [1]

Kane Quantum Computing Architecture [2]

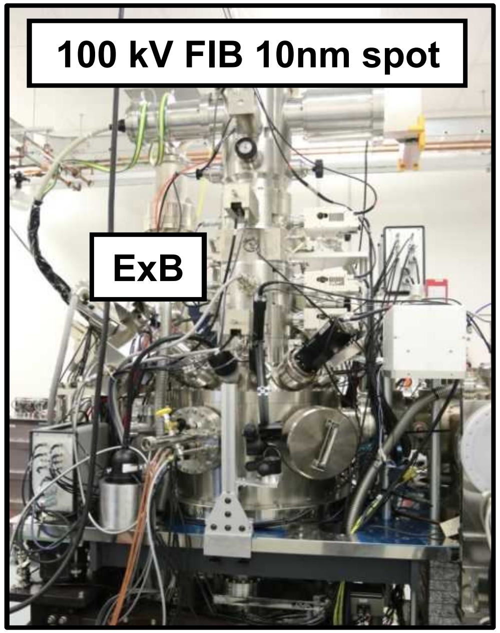


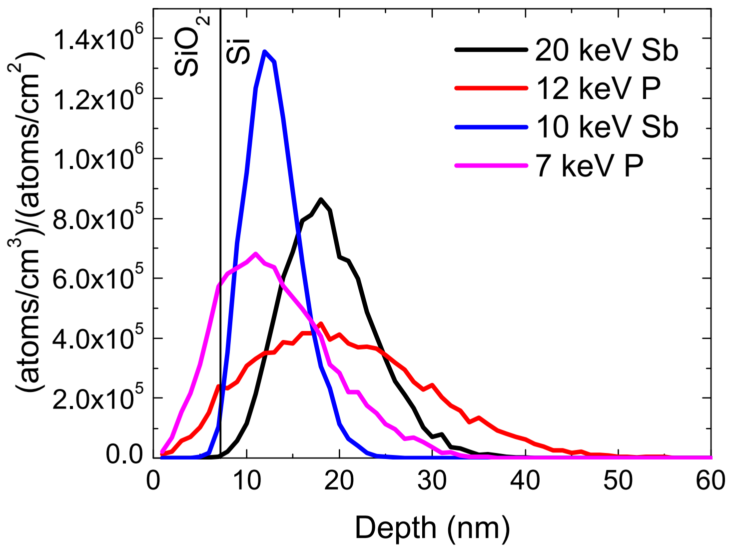
- Si environment allow leverage of vast existing fabrication capability
  - Si substrate shields qubit from spin and charge: "semiconductor vacuum" [2]
- P Donors in Si have very long spin coherence times [3]
  - ^{31}P nuclear spin coherence time > 30 s
  - e^- spin coherence time > 0.5 s

[1] http://qoqms.phys.strath.ac.uk/research_qc.html [2] Kane, *Nature*, **393** (1998);
[3] Steger, *Science*, **336** (2012); [4] Muhonen, *Nat. Nano.*, **9** (2014)

Routes to Single Donors in Si

Ion Implantation





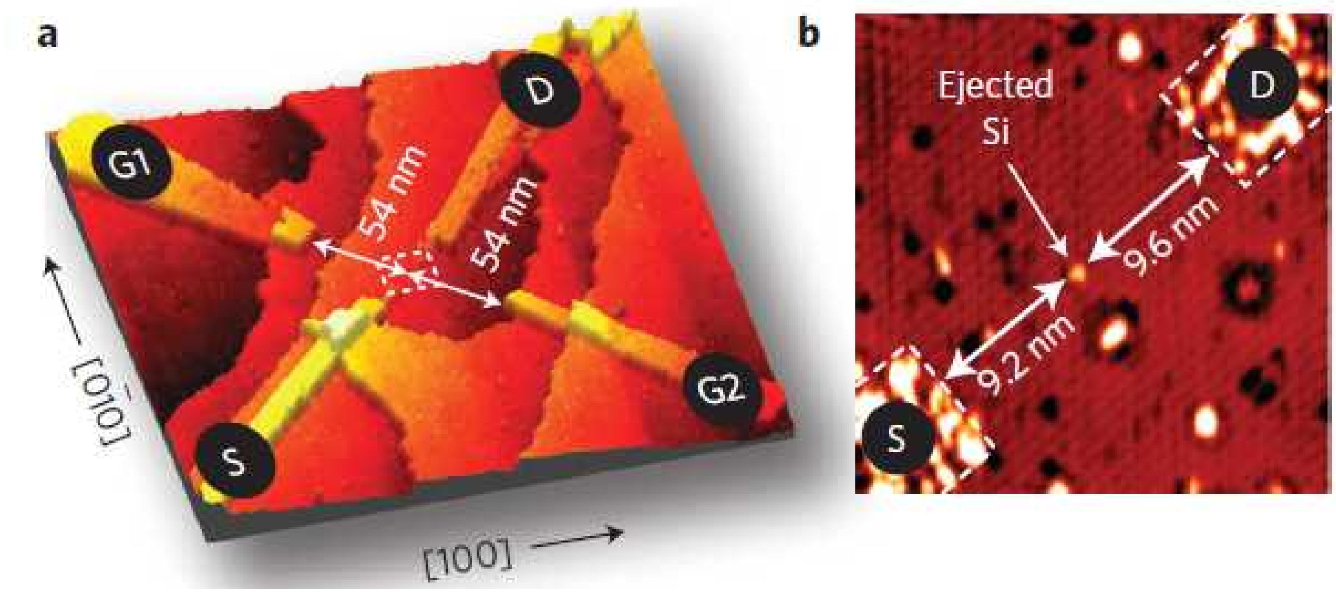
Provided courtesy of Bielejec (Sandia National Laboratories)

- Straggle: Significant uncertainty in donor placement

Routes to Single Donors in Si

Atomically Precise Donor Placement

Single Atom Transistor

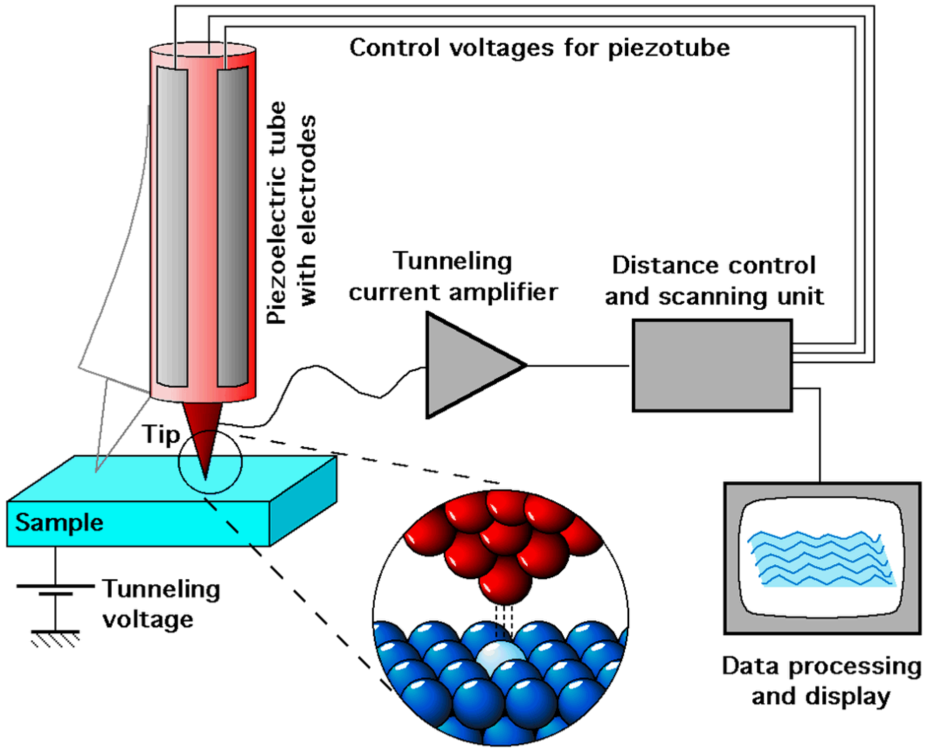


Fuechsle, *Nat. Nano.*, 7 (2012)

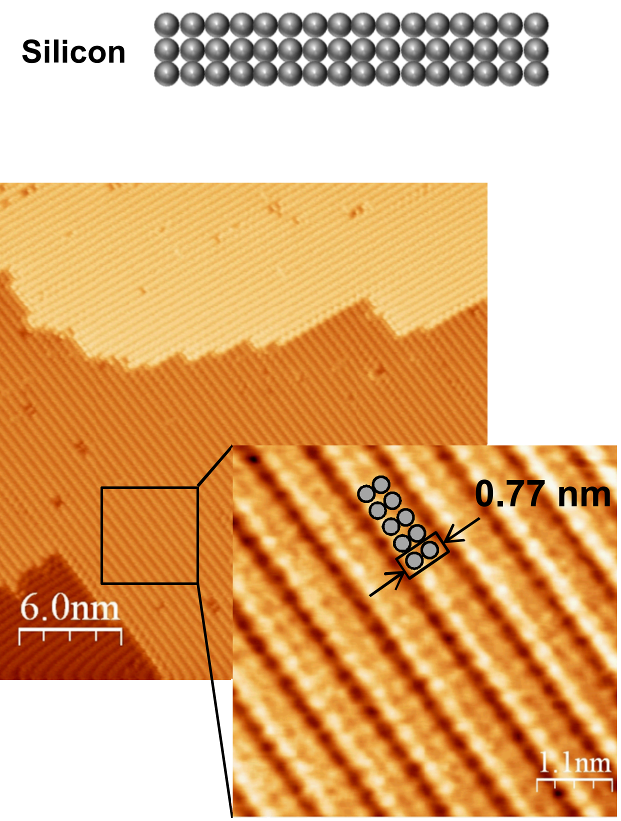
- Simmons' group (UNSW) has demonstrated atomically precise donor placement for device fabrication

Scanning Tunneling Microscopy

STM Schematic

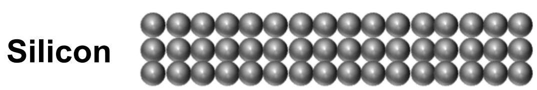


Si(100) – 2×1 Surface

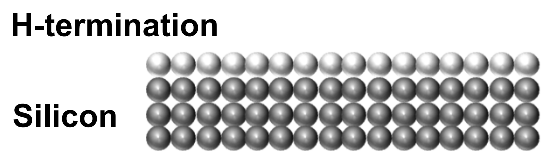


STM Hydrogen Lithography

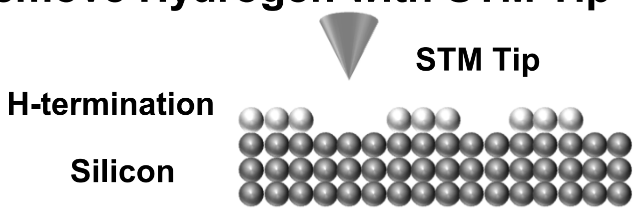
Si(100) – 2×1:H Surface

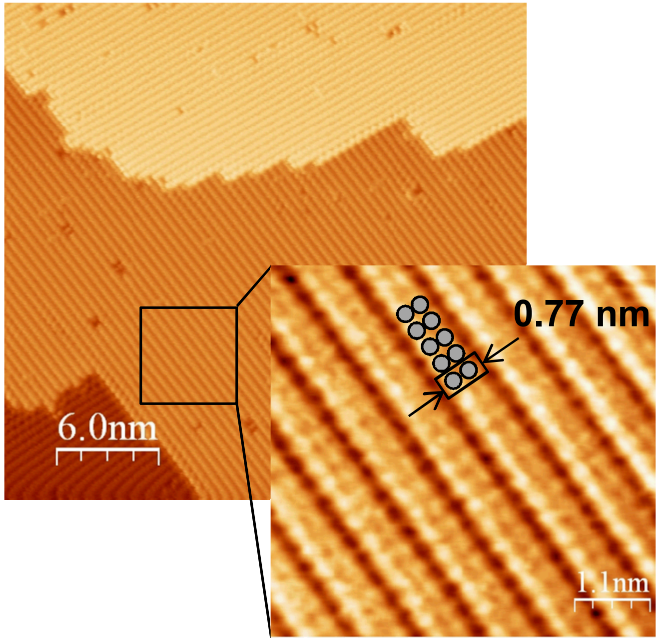


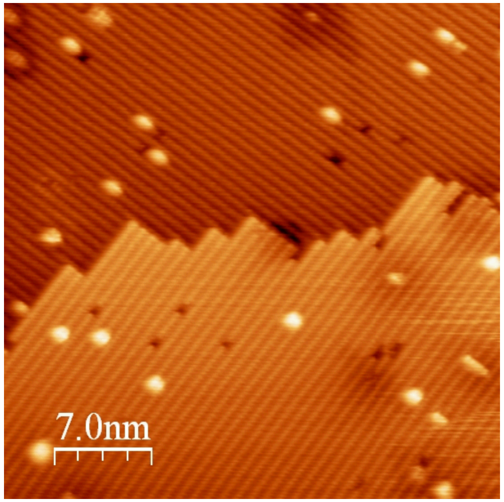
Si(100) – 2×1:H Surface



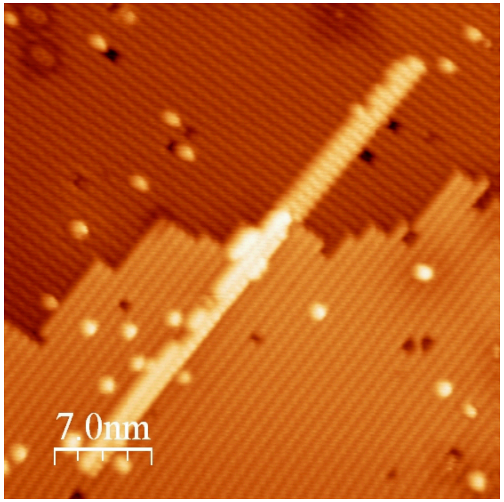
Remove Hydrogen with STM Tip







Dark spots are missing Si atoms.
Bright spots are missing H atoms



Can selectively remove H from the Si(100) – 2×1:H Surface using the STM tip

Donor Placement by STM Hydrogen Litho

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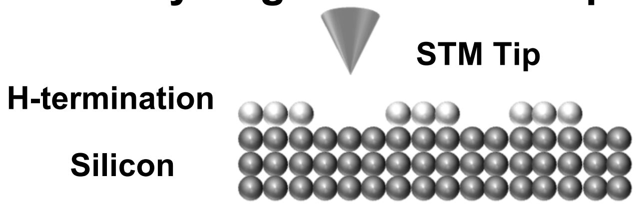
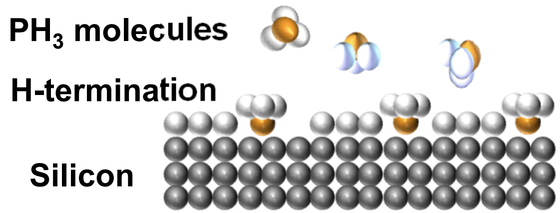
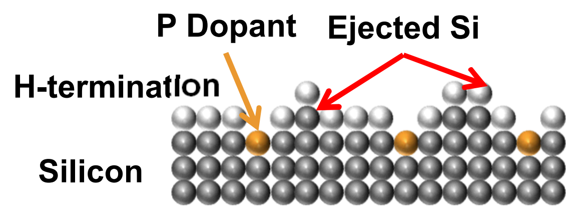
Remove Hydrogen with STM Tip

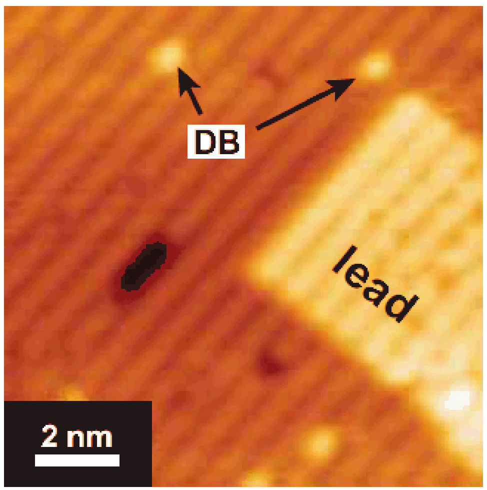


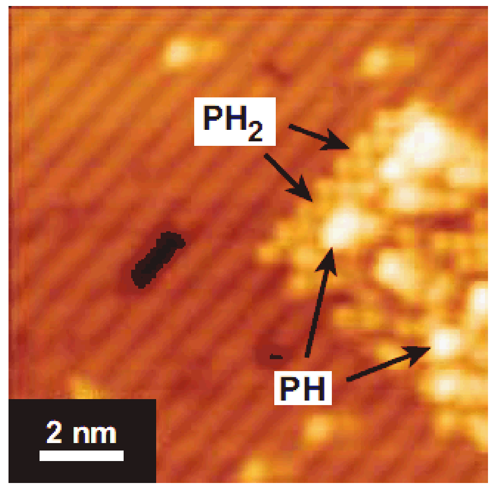
Dose sample with PH_3

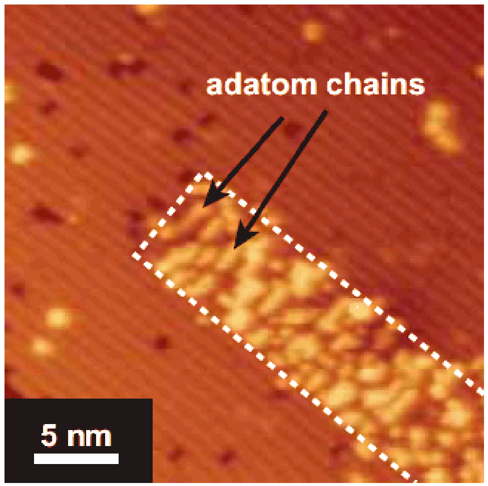


Incorporate P Dopants

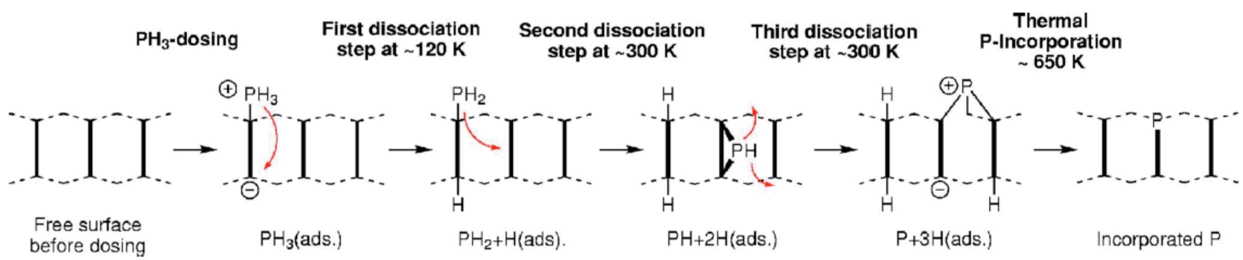








[1] Fuechsle, *Ph.D. Dissertation* (2011)



[2] Wilson, *Phys. Rev. B*, **74** (2006)

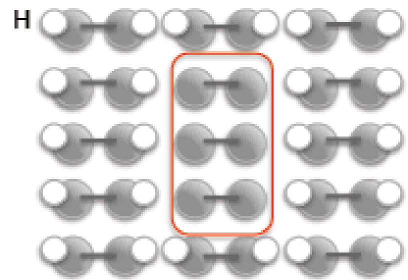
Substitutional incorporation of P donors from PH_3 is a thermally activated process

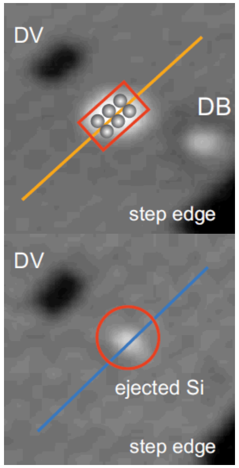
Factors Limiting Single Donor Placement Yield

Single Donor Yield = Litho Yield × Chemistry Process Yield

- STM Lithographic Pattern Size
    - Highest reported *single* donor yield for 1x3 dimer lithography patterns [1].

Target Litho Pattern Size: <u>1x3 Dimers</u>

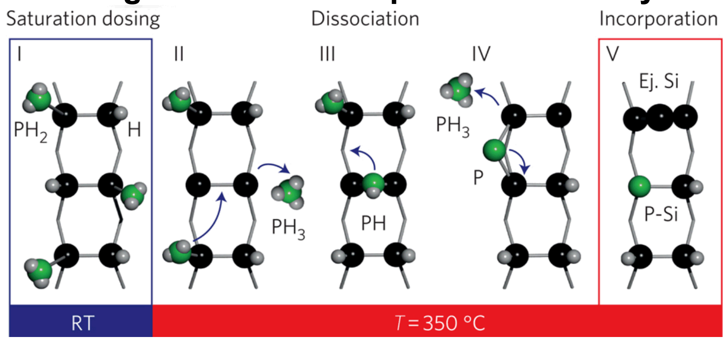




[1]

- Chemical Pathway
    - Reported 70% yield for single donors in 1x3 dimer patterns [1]

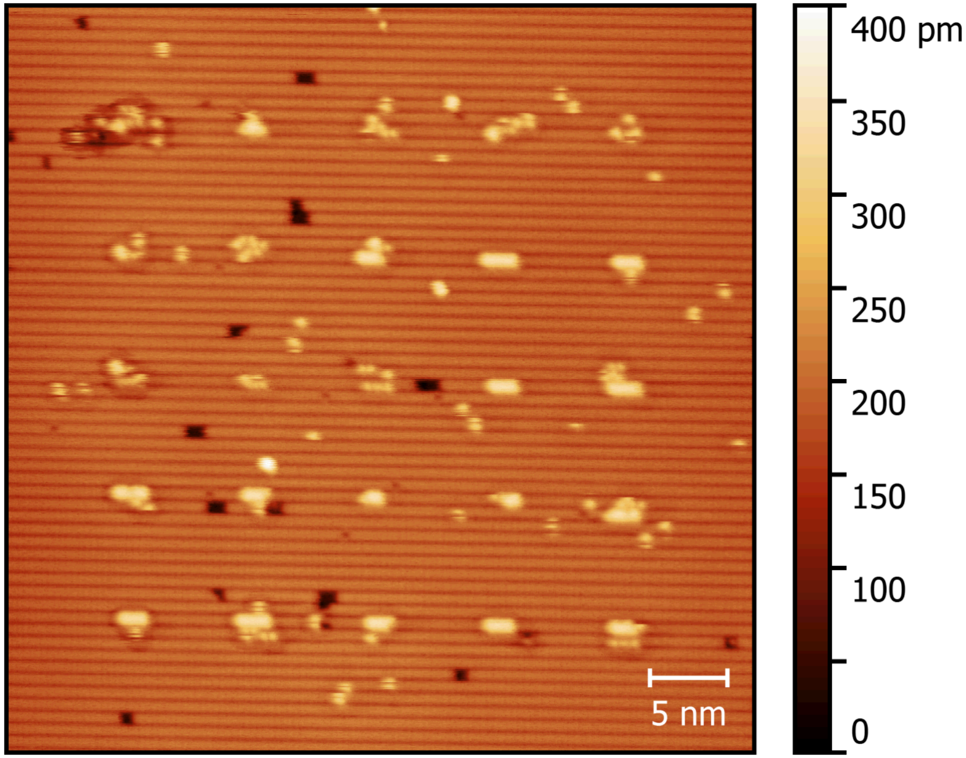
Single P Donor Incorporation Pathway



[2] Fuechsle, *Nat. Nano.*, 7 (2012)

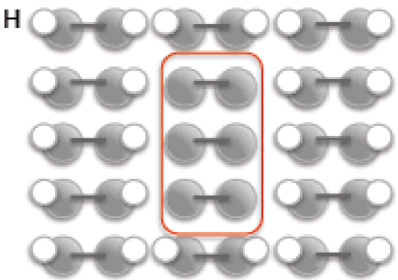
[1] Fuechsle, *Ph.D. Dissertation* (2011)

Lithography at Few Atom Limit



Only 20% of Litho Sites Single Row

Target Litho Array Element: 1x3 Dimers

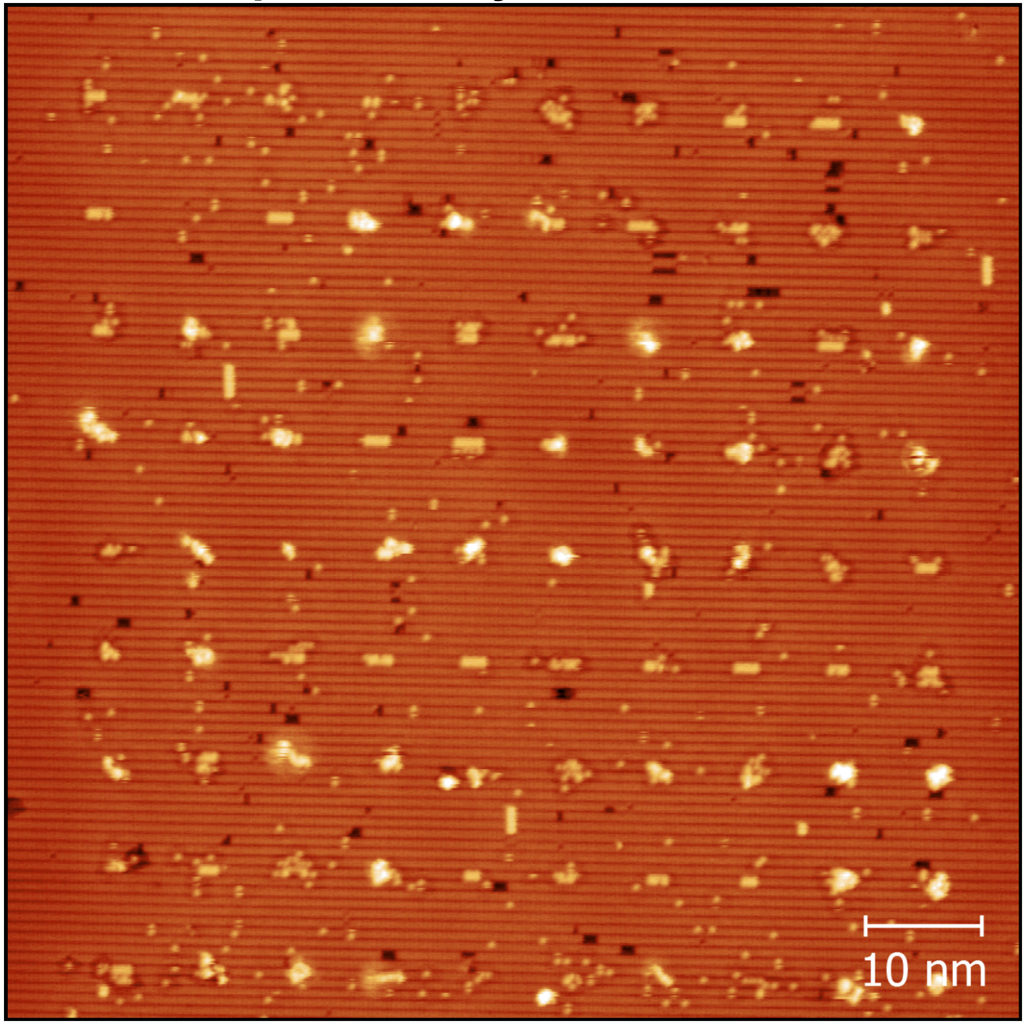


- Examine lithography statistics
- Factors affecting litho yield:
  - STM tip sharpness & stability
  - Litho Process Parameters

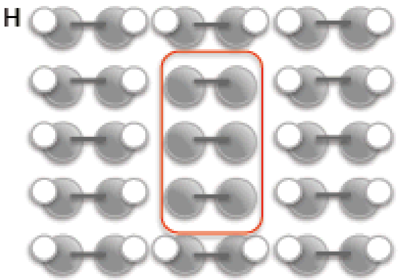
Limitations to Lithography at Few Atom Limit

Sandia National Laboratories

Effect of Tip Instability



Target Litho Array Element: 1x3 Dimers



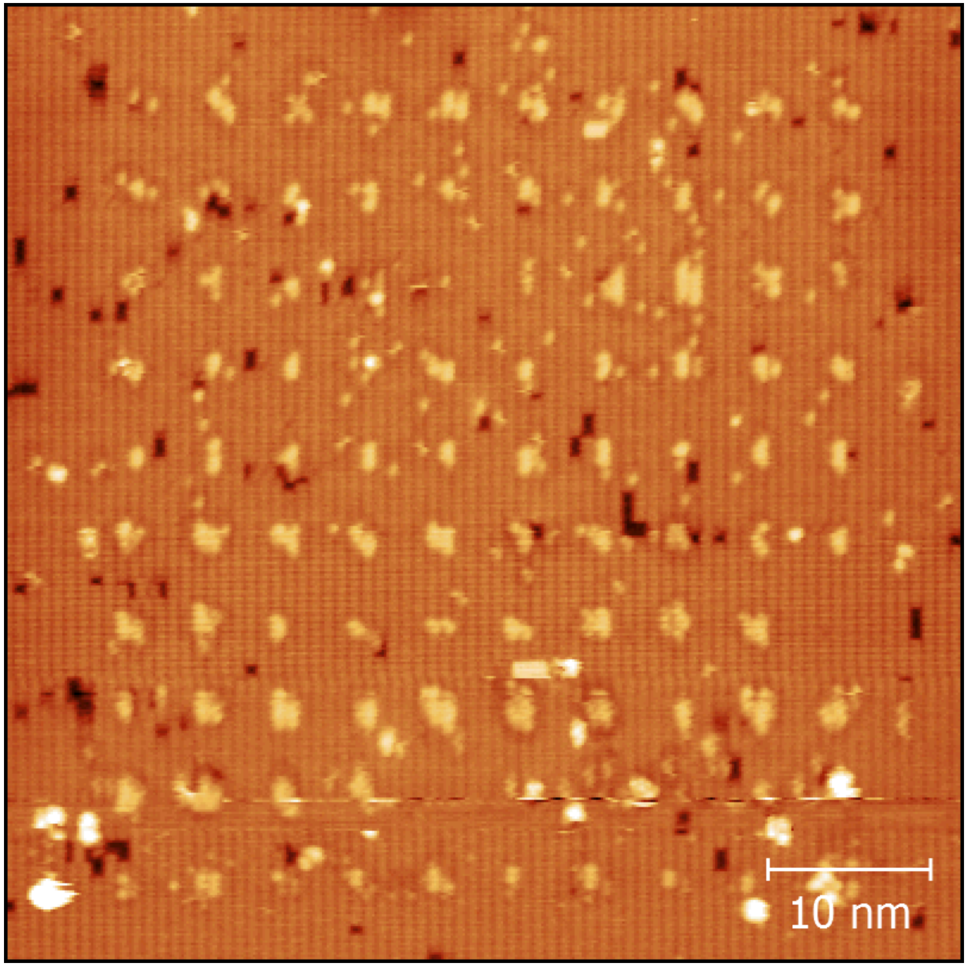
Unstable tips: **(1) drop material during patterning**
(2) give disordered lithographic patterns

Limitations to Lithography at Few Atom Limit

Sandia National Laboratories

Effect of Tip Alignment to Dimer Rows

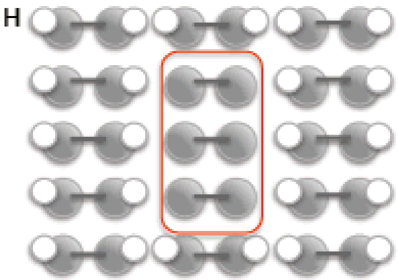
Litho Sites Intentionally Rotated 45° from Alignment with Dimer Rows



Only 10% of Litho Sites Single Row

Data collected by R. Butera (LPS)

Target Litho Array Element: 1x3 Dimers

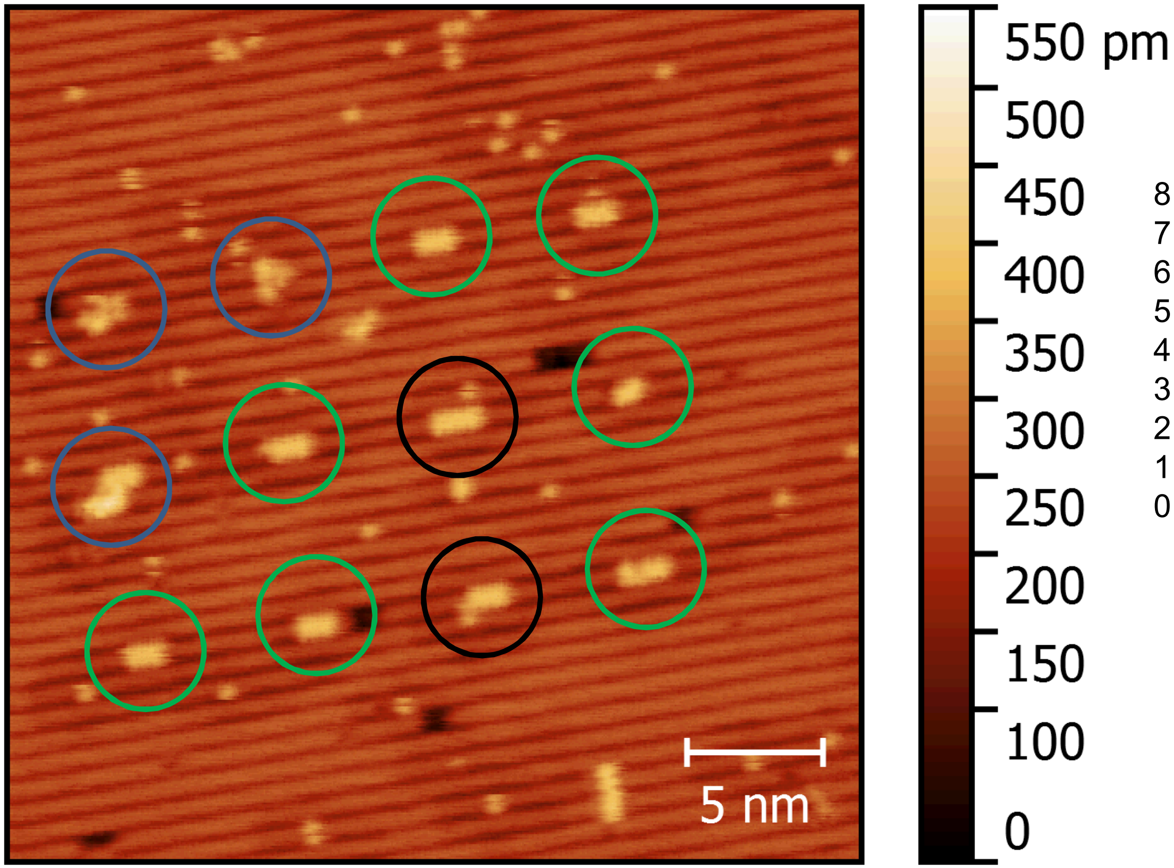


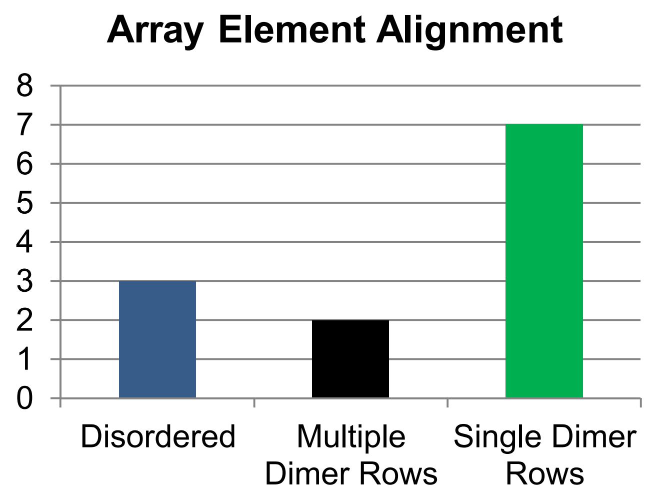
Lithographic Arrays – Better Alignment

Sandia National Laboratories

Steps to improve litho yield:

(1) Reduce Array Size to Improve Alignment to Dimer Rows
(2) Consistent Tip Preparation

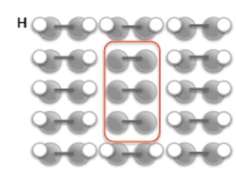




Single Dimer Row Yield: 7/12

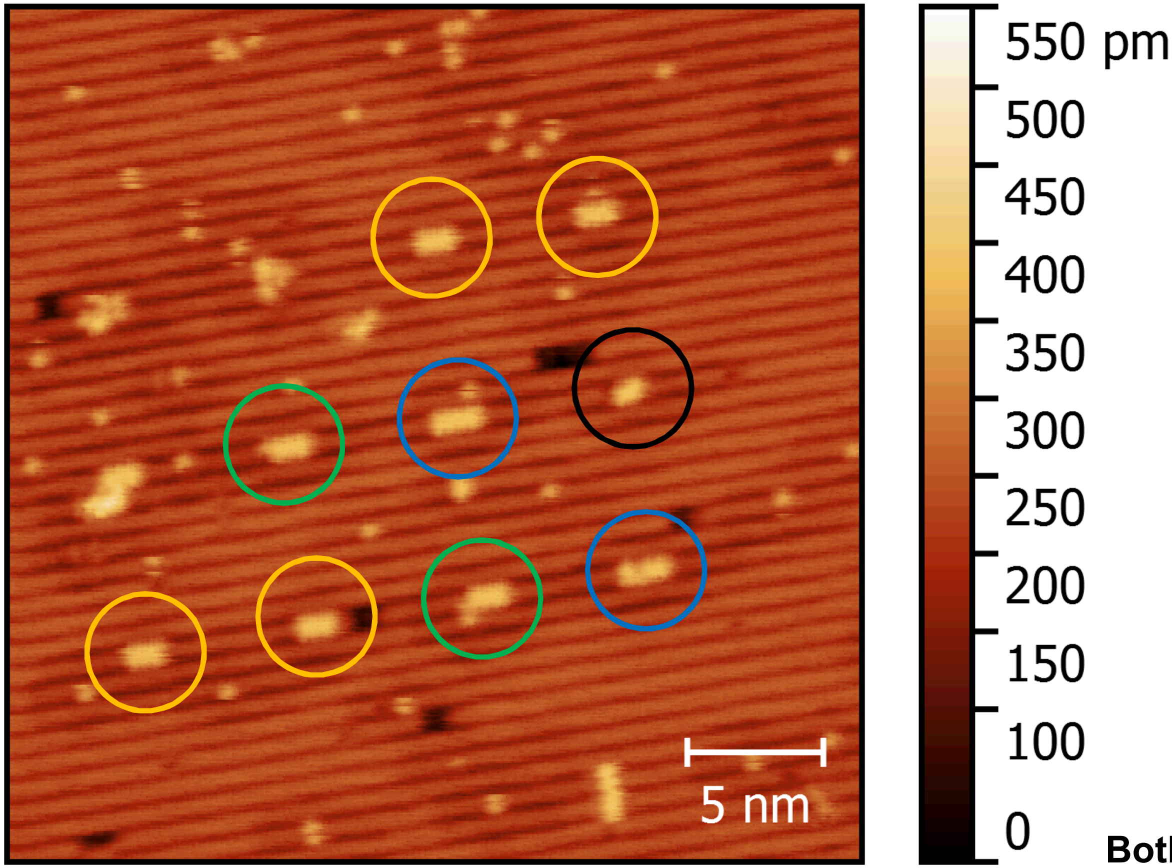
Litho Feature Legend: **Disordered Features**
Multiple Dimer Row Features
Single Dimer Row Features

Target Litho Array Element: 1x3 Dimers

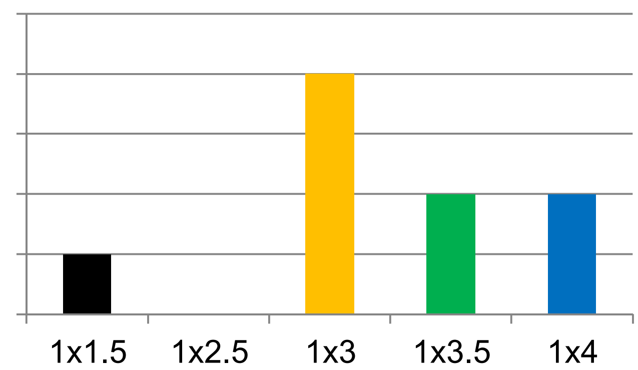


Lithographic Arrays – Better Yield

Reduced Array Size and Consistent Tip Preparation



Single Dimer Row Pattern Length (Dimers)

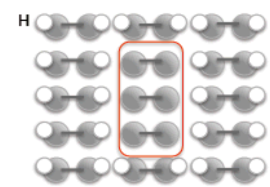


Yield of 1x3 Dimer Patters: 4/12
Both 1x3 and 1x3.5 Dimer Patterns: 6/12

Litho Feature Legend:

1x1.5 Dimers
1x2.5 Dimers
1x3 Dimers
1x3.5 Dimers
1x4 Dimers

Target Litho Array Element: 1x3 Dimers



P Donor Incorporation in Lithographic Arrays

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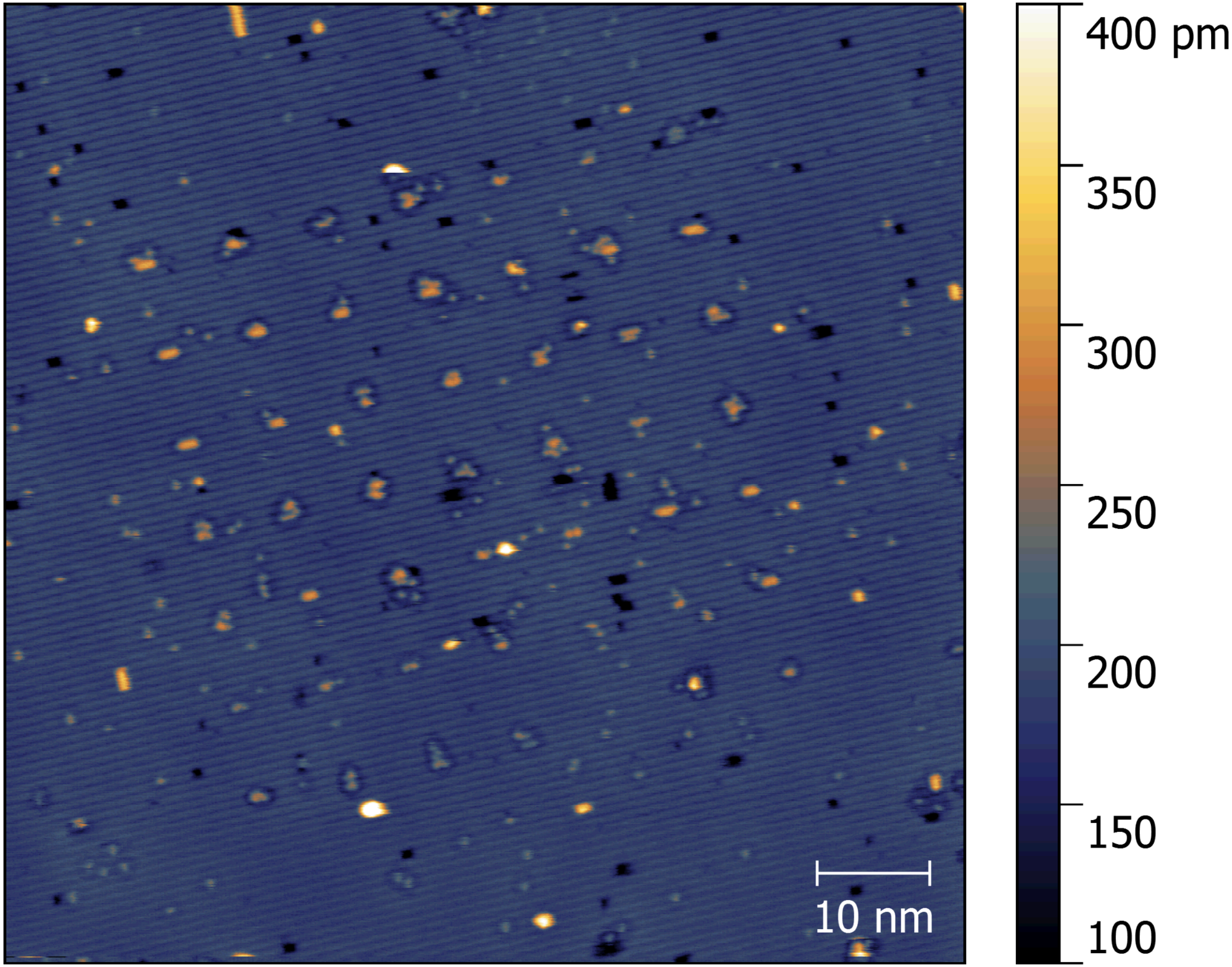
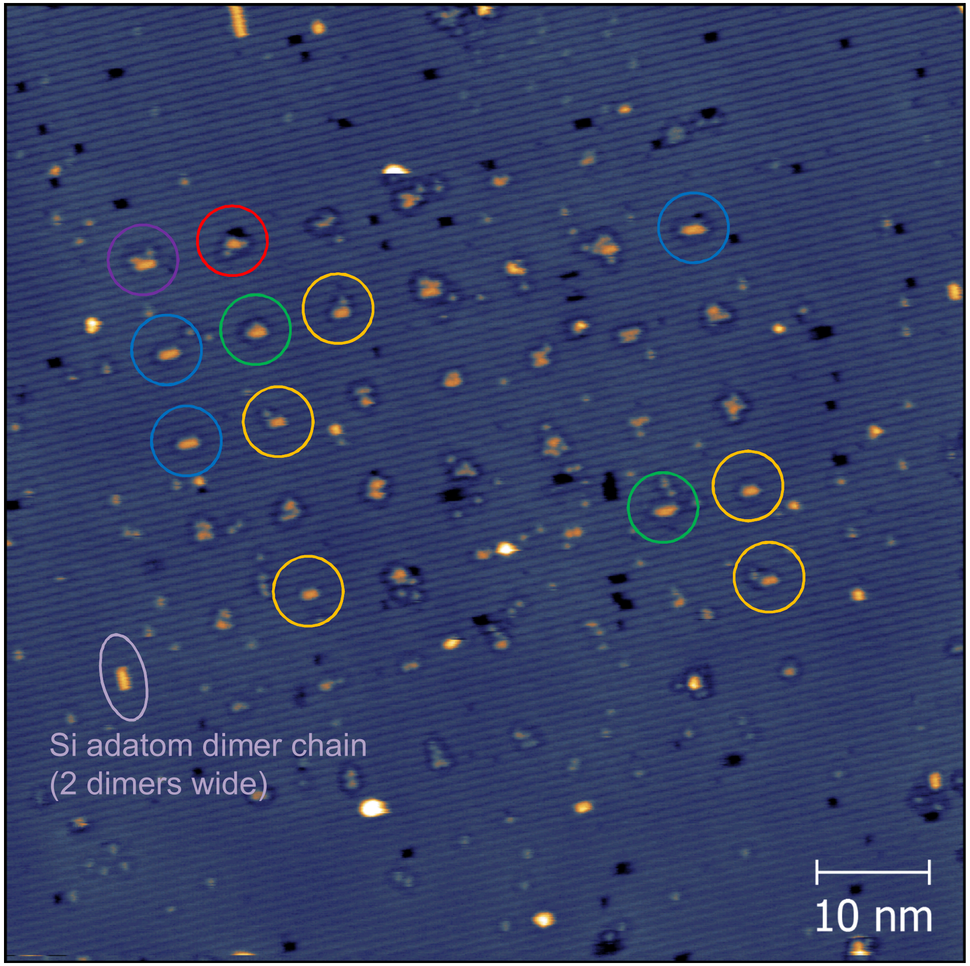
7x7 Litho Array

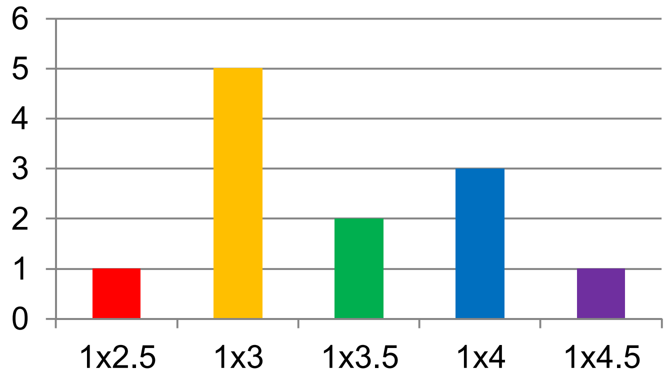


P Donor Incorporation in Lithographic Arrays



1x2.5 Dimers
1x3 Dimers
1x3.5 Dimers (extra dangling bond)
1x4 Dimers
1x4.5 Dimers (extra dangling bonds)

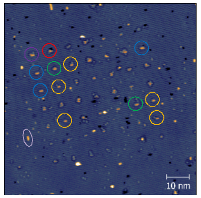
Single Dimer Row Pattern Length (Dimers)



Yield of 1x3 Dimer Patters: 5/49 (~10%)
Both 1x3 and 1x3.5 Dimer Patterns: 7/49 (~15%)

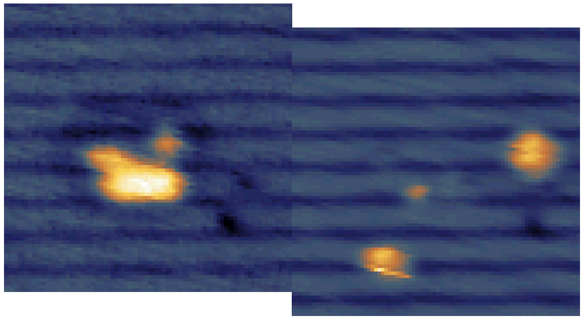
Analysis of P Donor Incorporation in Arrays

7x7 Litho Array

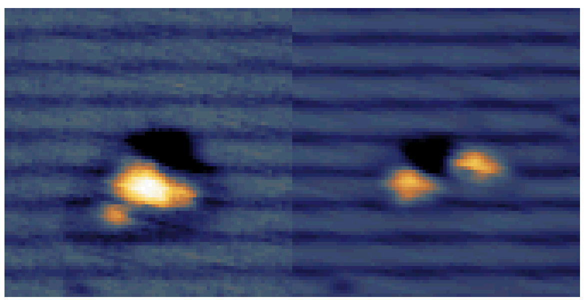


Post Litho | Post PH_3 Dose & Incorporate

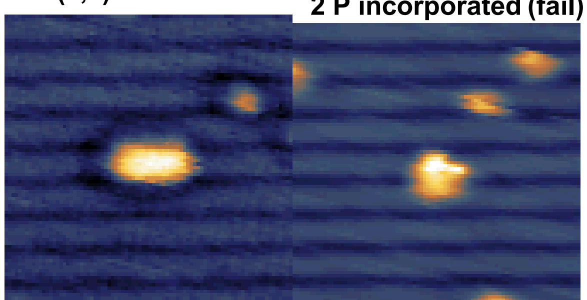
Element (1,1): 1x4 Dimers (+dangling bonds) | Single Si-P heterodimer



Element (1,2): 1x2.5 Dimers | Dangling Bonds: Fail

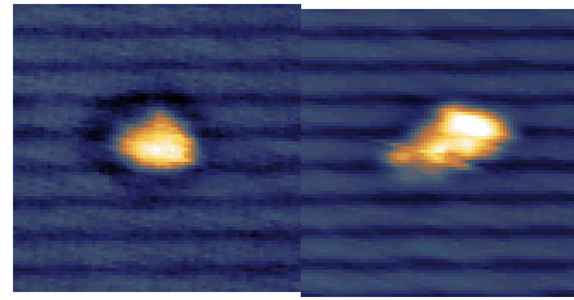


Element (2,1): 1x4 Dimers | Pair of ejected Si adatoms: 2 P incorporated (fail)

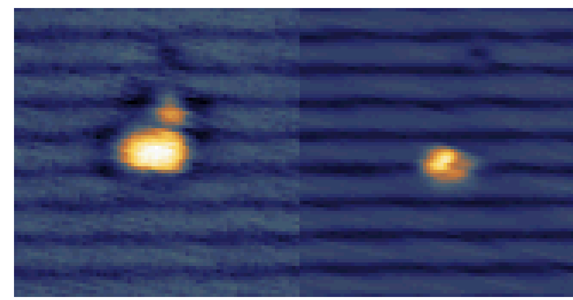


Post Litho | Post PH_3 Dose & Incorporate

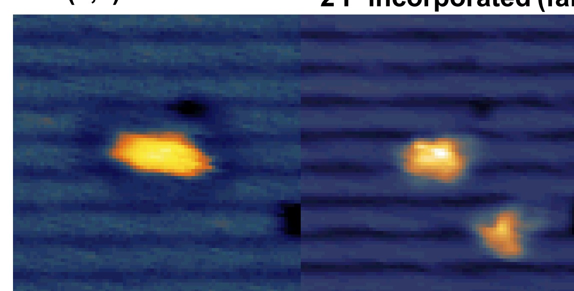
Element (2,2): 1x3.5 Dimers | Unknown feature: Fail



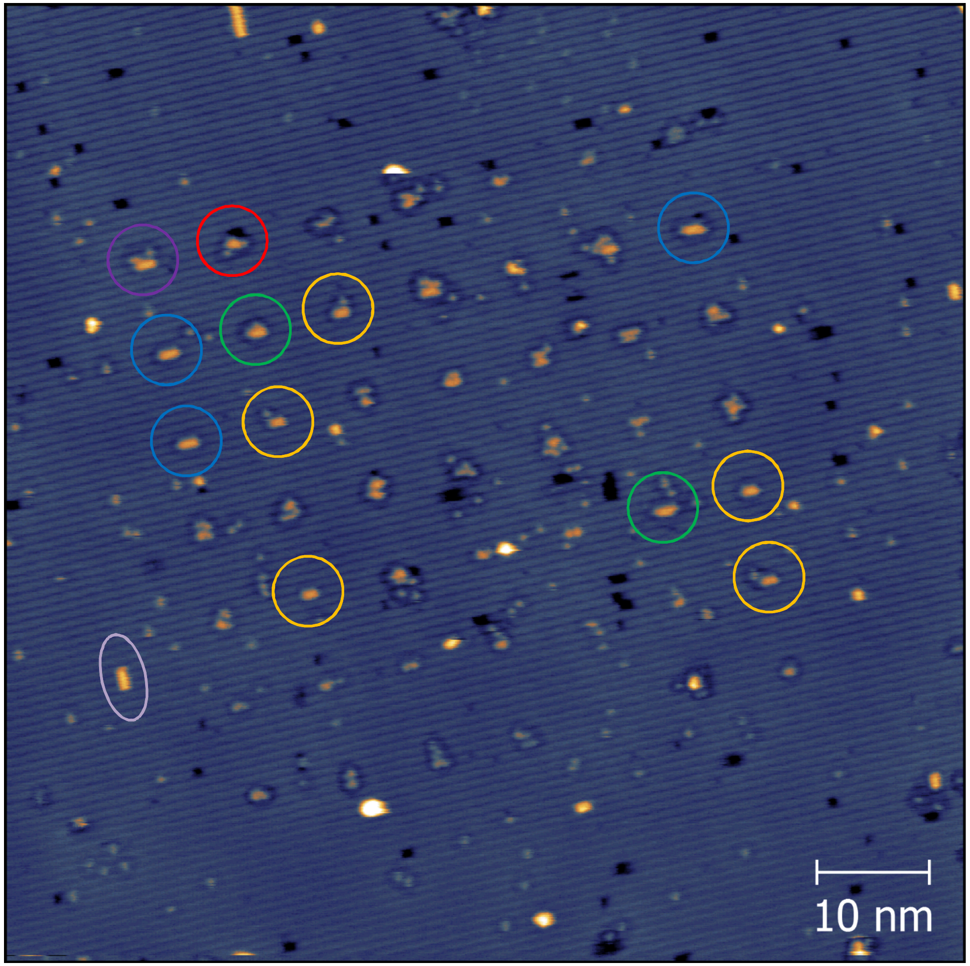
Element (2,3): 1x3 Dimers | Single Ejected Si



Element (2,7): 1x4 Dimers | Pair of ejected Si adatoms: 2 P incorporated (fail)



P Donor Yield in Lithographic Arrays



1x2.5 Dimers
1x3 Dimers
1x3.5 Dimers (extra dangling bond)
1x4 Dimers
1x4.5 Dimers (extra dangling bonds)

Incorporation Summary

Single Donor Incorporation:

- (1,1), (2,3), (3,2), (5,6), (5,7)

Double Donor Incorporation:

- (2,1), (2,7), (3,1), (6,7)

Unknown:

- (2,2)

Nothing:

- (1,2), (5,2)

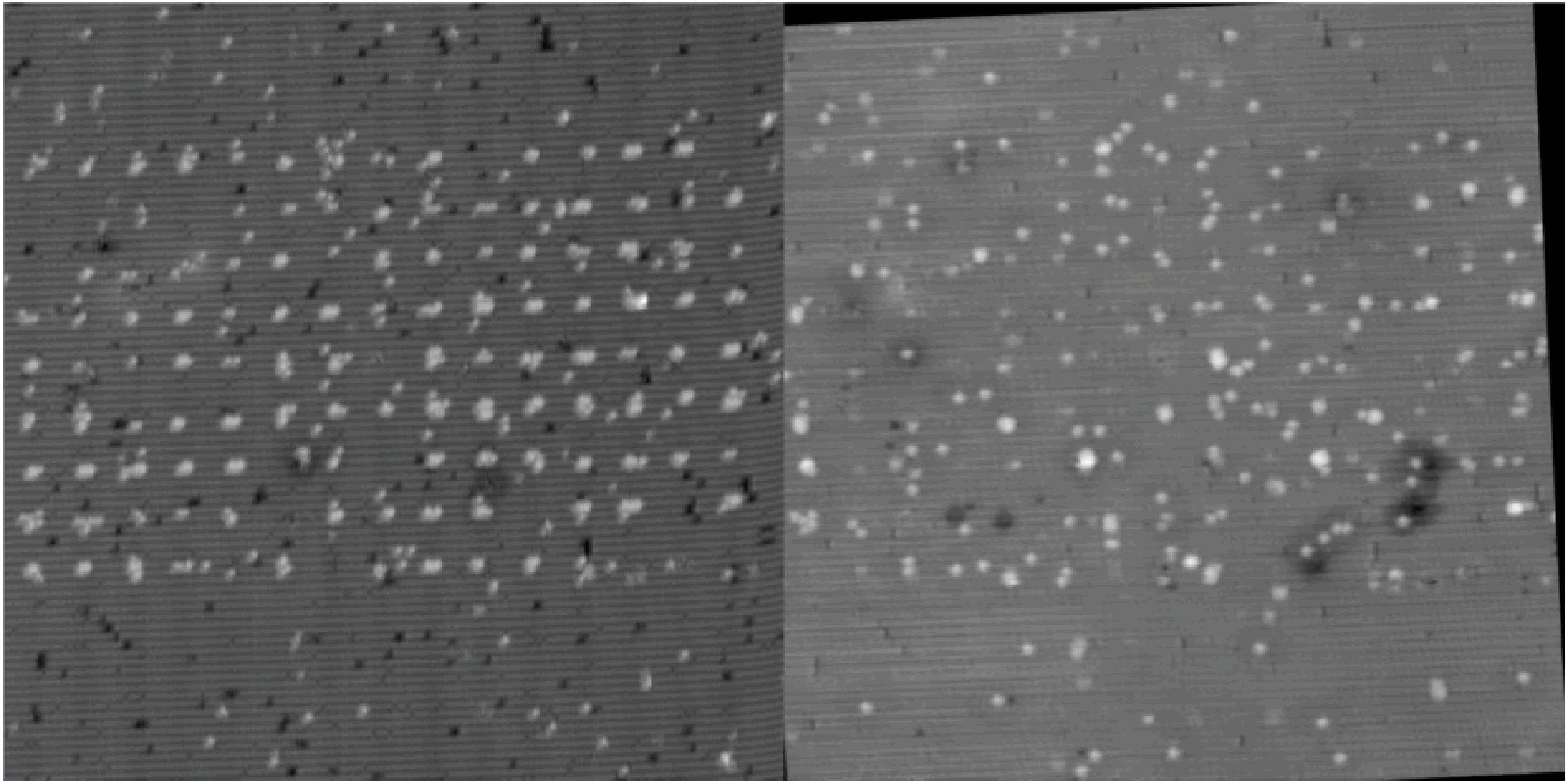
Single P yield for array: ~10% **(5/49)**

Single P incorporation for only 1x3 dimer sites : 60% **(3/5)**

Feature Identification for Array Analysis

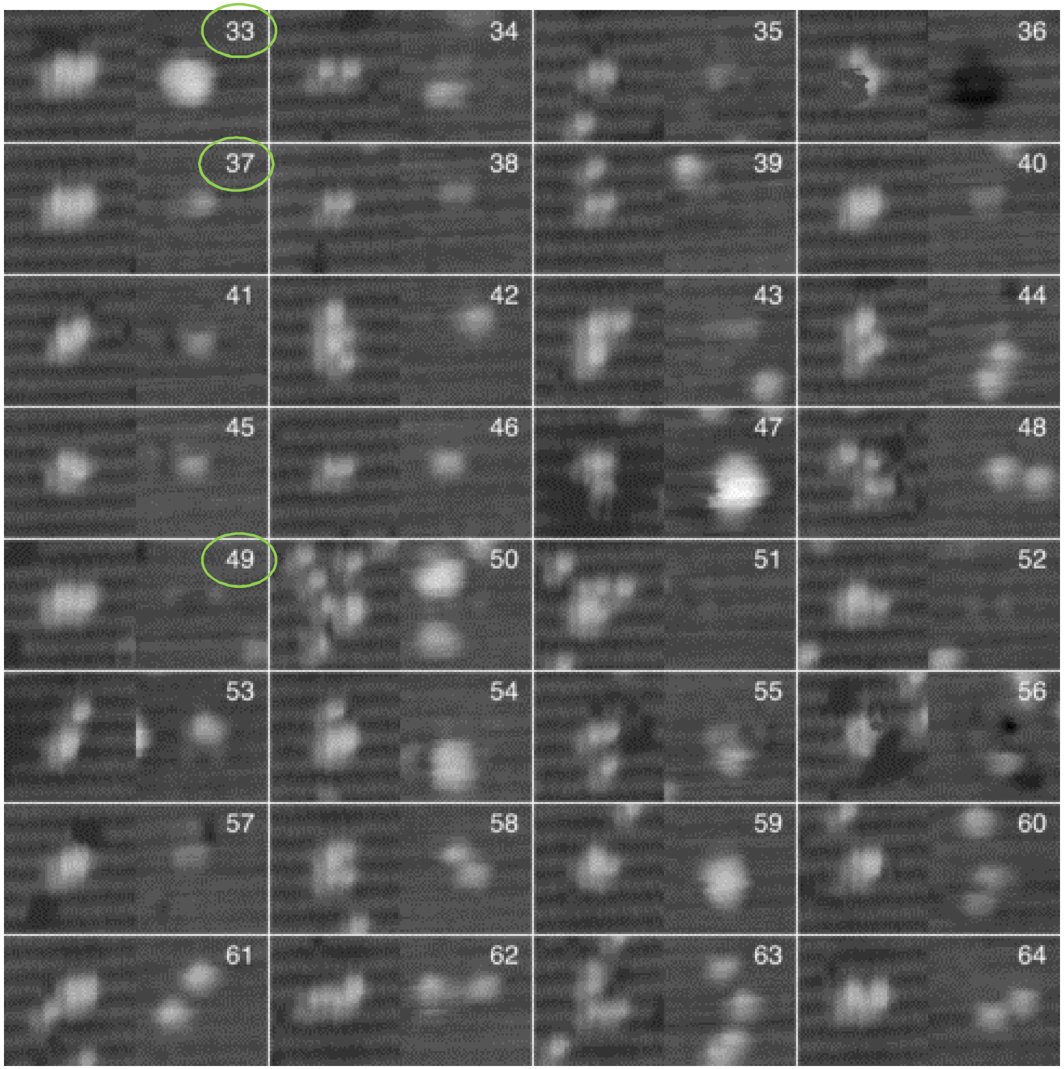
9x15 Lithographic Array, 100 nm x 100 nm

After PH_3 Dose and Incorporation



Align scan after lithography and scan after PH_3 dose and incorporation

Feature Identification in Incorporated Arrays



Compare post-lithography and post PH_3 dose and incorporation.
Did P incorporation happen at the litho sites?

P Donor Yield in Lithographic Arrays

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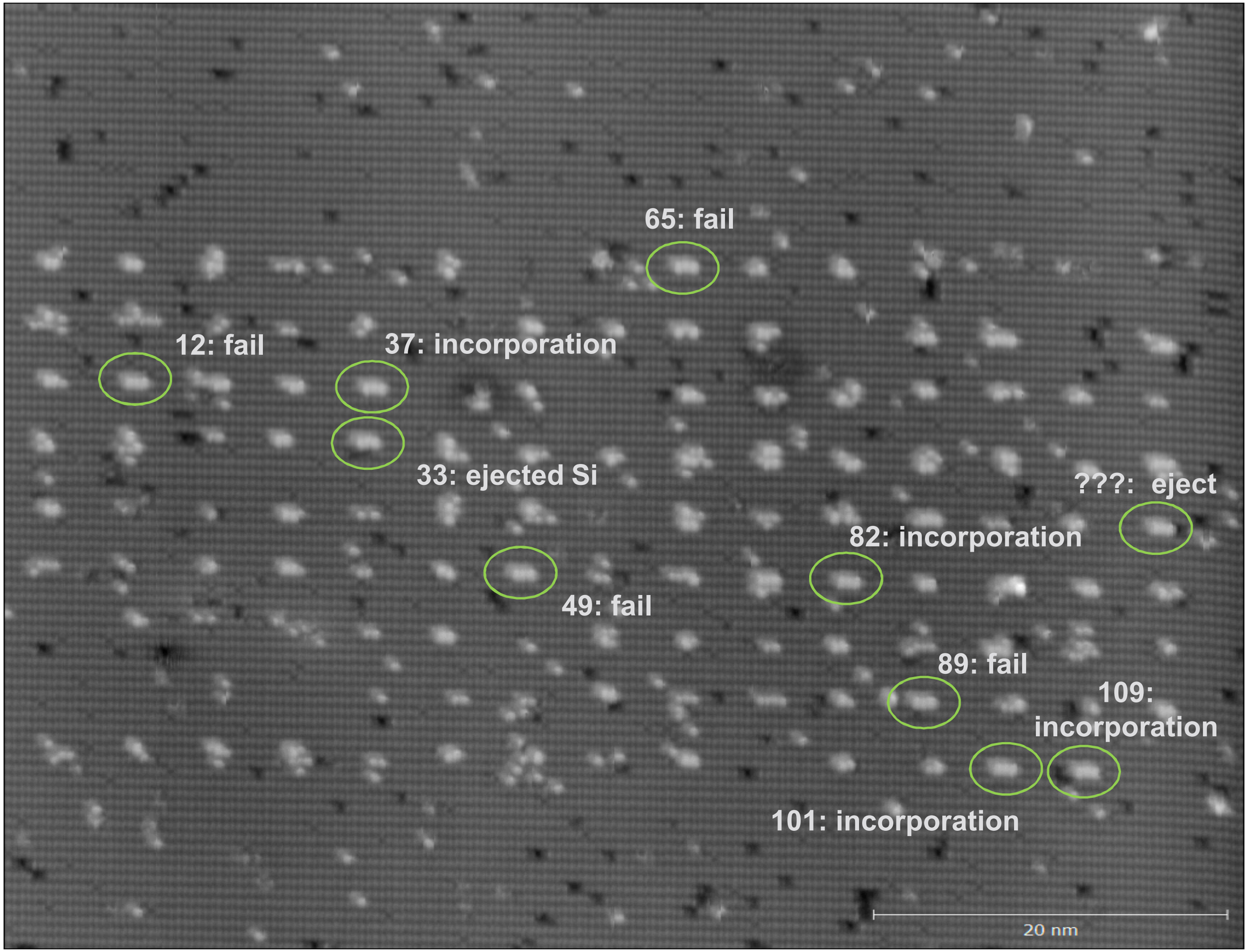
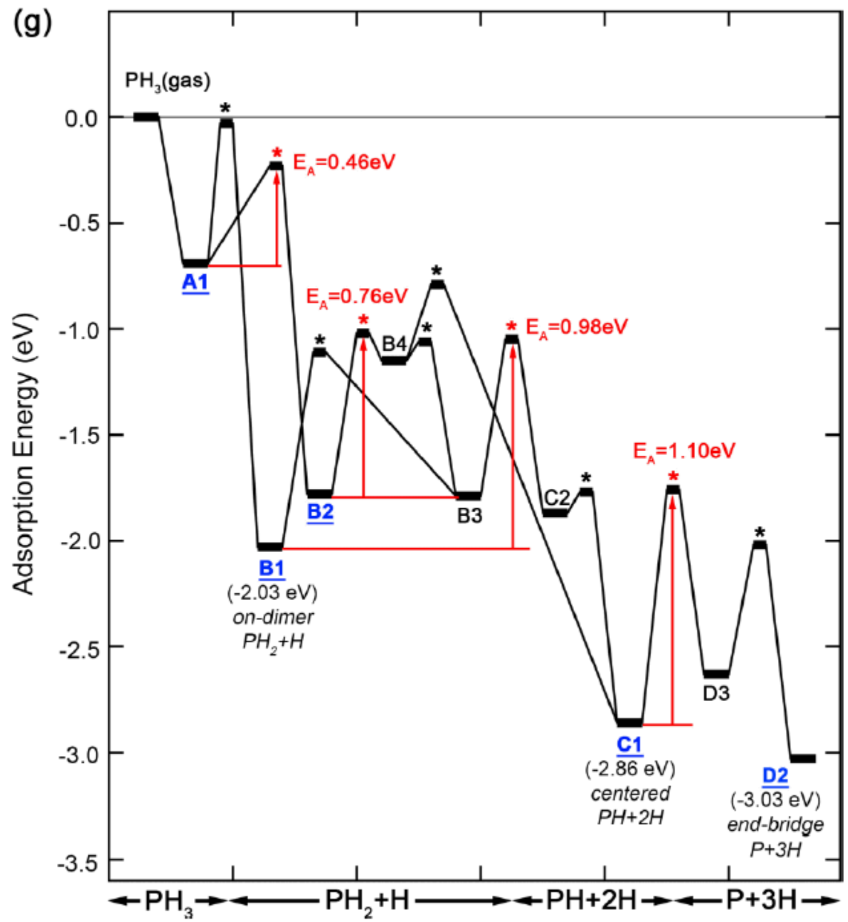


9x15 Litho Array. 10 out of 135 (7%) sites successful 1x3 dimer patches.
7 incorporated 1x3 dimer litho sites out of 135: *<u>5% single donor yield for array</u>*.
7 incorporated sites out of 10 1x3 dimer litho sites: *<u>70% incorporation in 1x3 dimer patches</u>*.

Simulations of P Donor Incorporation

Sandia National Laboratories

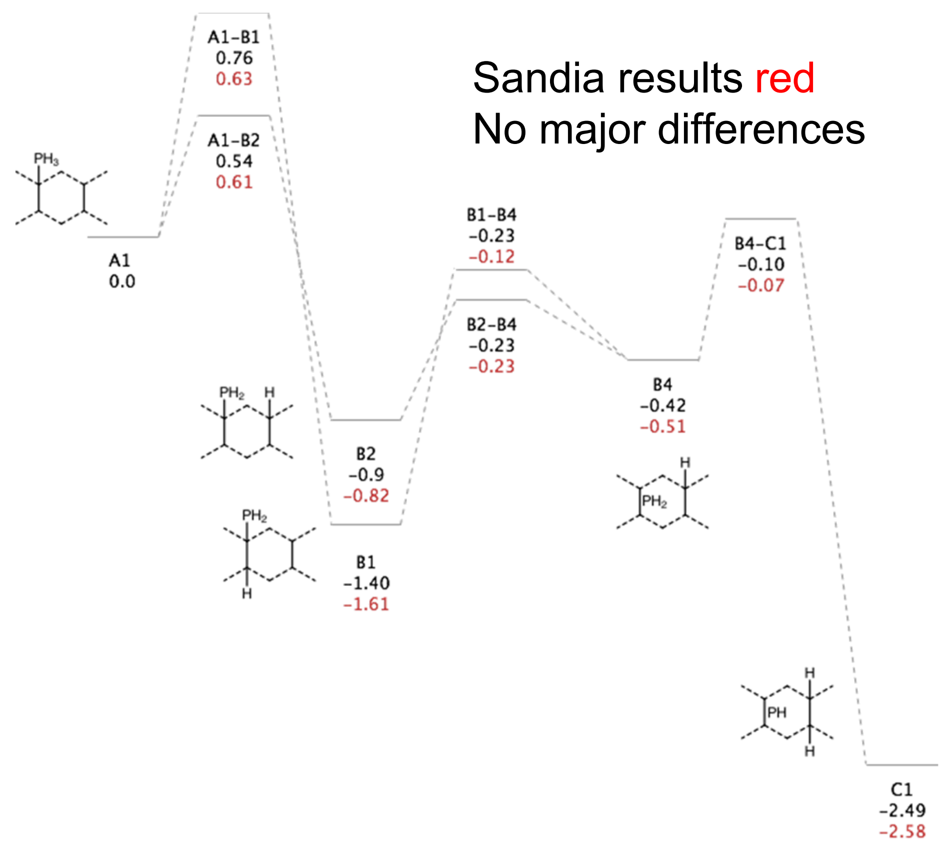
Calculated PH_3 Dissociation Reaction Barriers



Warschkow, *J. Chem. Phys.*, 144 (2016)

Sandia results red

No major differences

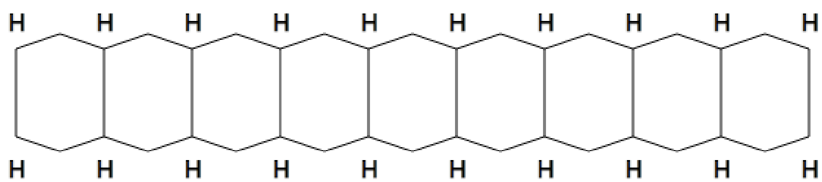


Muller, Schultz, Baczewski (Sandia)

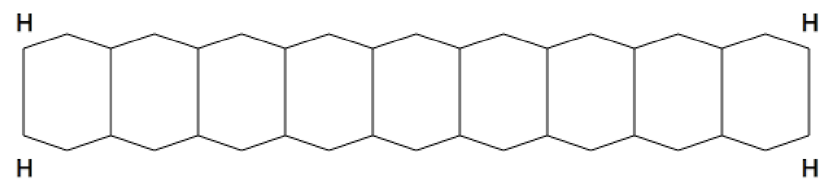
Kinetic Monte Carlo Simulations of P Incorporation

KMC is an algorithm to rapidly sample a chemical mechanism to generate probable resulting product states.

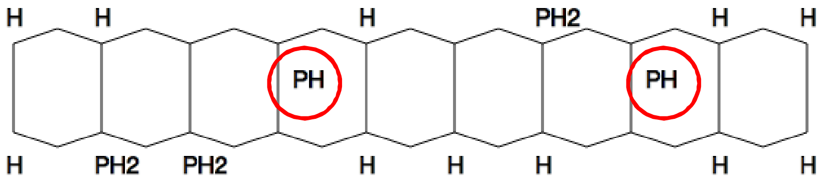
Create a row of N dimers (here N=10)



Depassivate the interior dimers



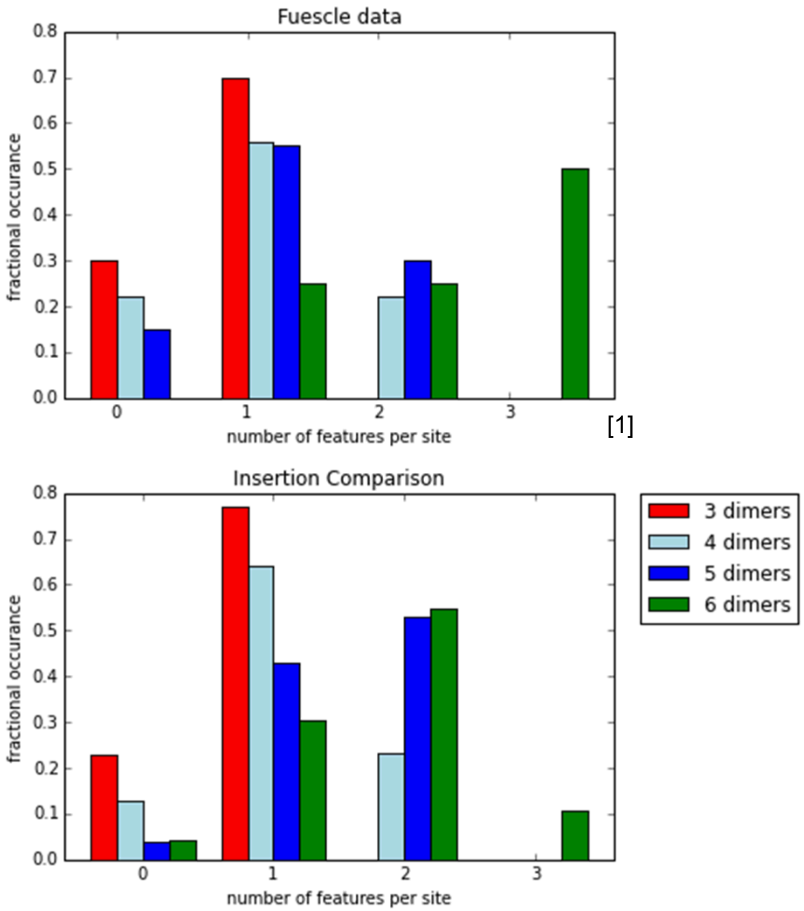
Sample the chemistry until the surface is saturated

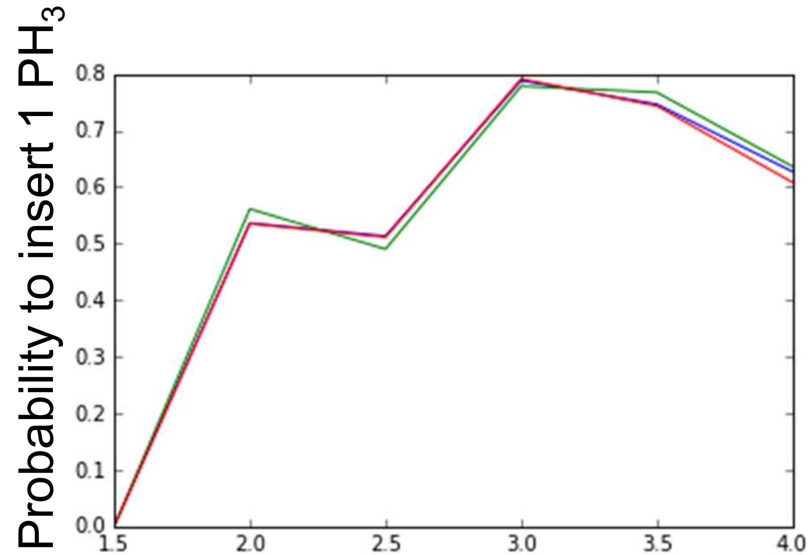


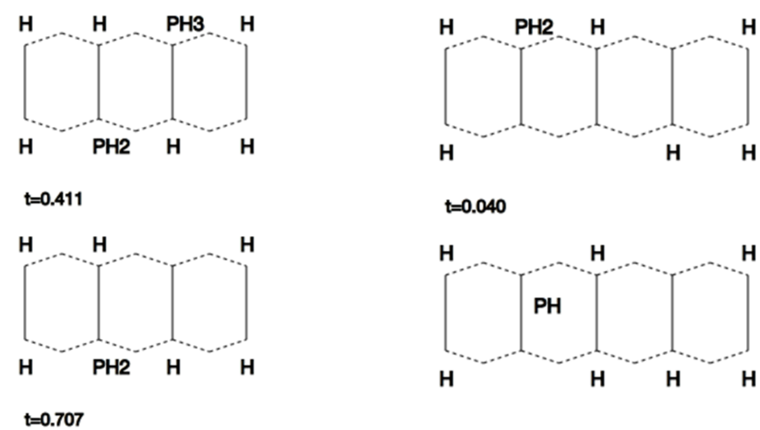
Bridging PH groups lead to P incorporation

Kinetic Monte Carlo Simulations of P Incorporation in Lithographic Windows

Sandia National Laboratories







Values for 1x3 dimer lithographic windows similar to our experimental values (0.6 – 0.7).

[1] Fuechsle, *Ph.D. Dissertation* (2011)

Muller, Schultz, Baczewski (Sandia)

Summary

- Demonstrated STM Hydrogen Lithography at length scales necessary for placing single P donors

- Yield of 1x3 dimer patterns initially 0%.

- Increased yield to 10% in large arrays with better tip alignment.

- Better tip alignment for small arrays led to 1x3 dimer pattern yield up to 33%.

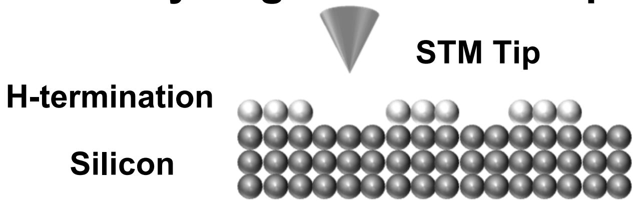
- Overall yield of single P donors for Arrays ~5-10%.

- Yield of single P donors only for 1x3 dimer features ~60% – 70%, very close to simulation values and prior experimental data.

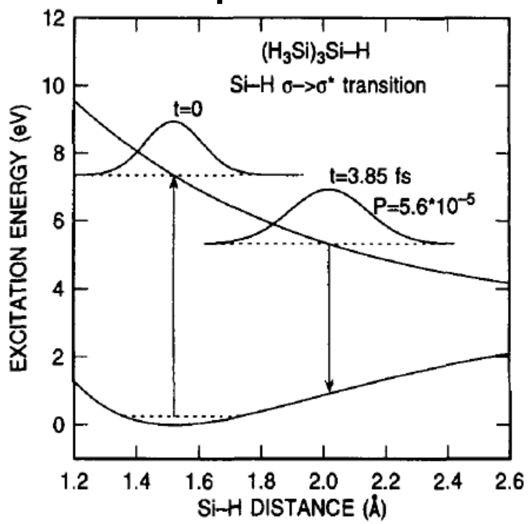
Extra Information

STM Hydrogen Lithography Mechanisms

Remove Hydrogen with STM Tip



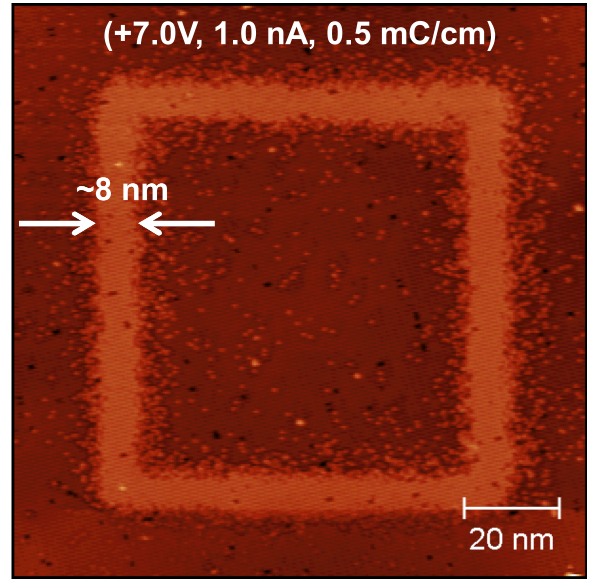
Two H Desorption Mechanisms

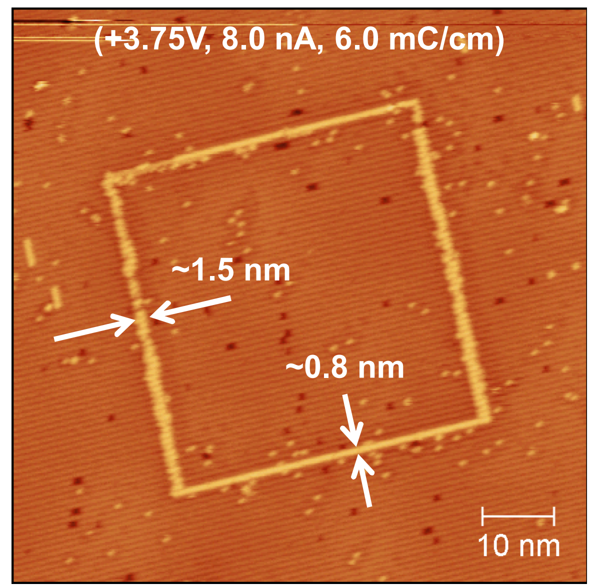


Avouris, *Chem. Phys. Lett.*, 257 (1996)

Multi-electron stochastic process

Tune pattern size with (V, I, dose) conditions

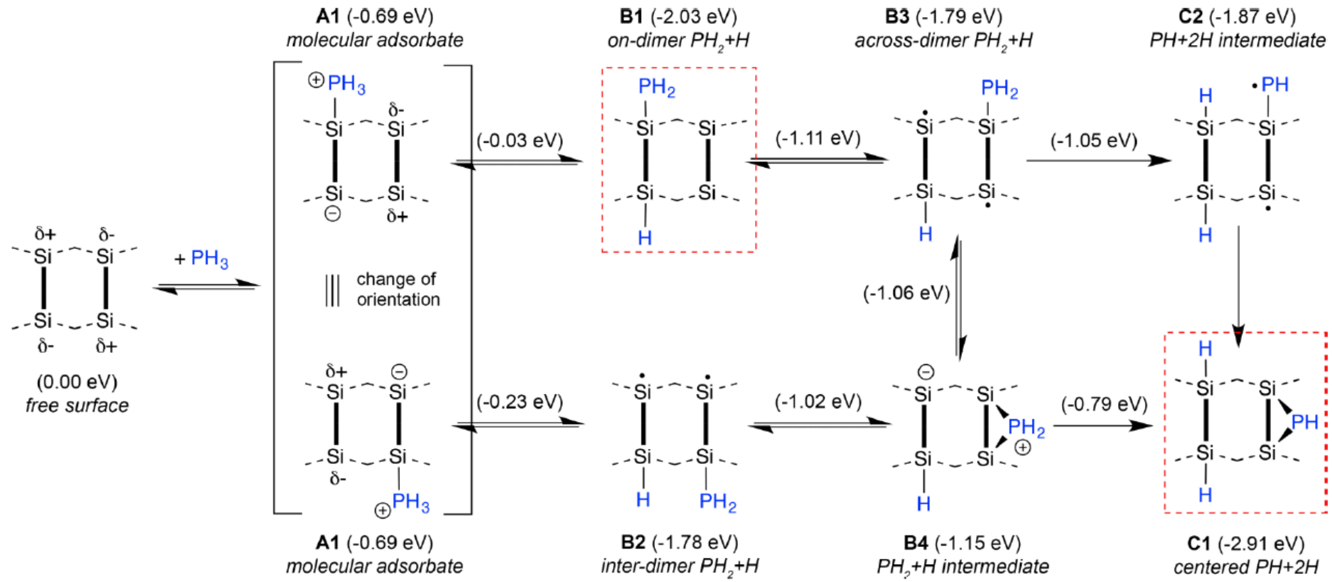




P Donor Incorporation Mechanism

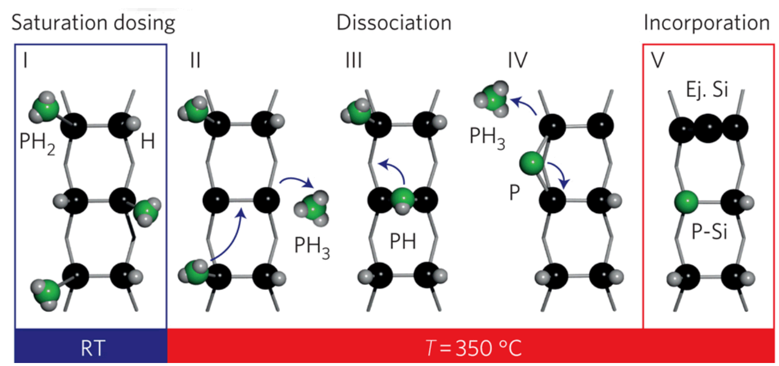
Sandia National Laboratories

Adsorption and Dissociation of PH_3 on Si(100)



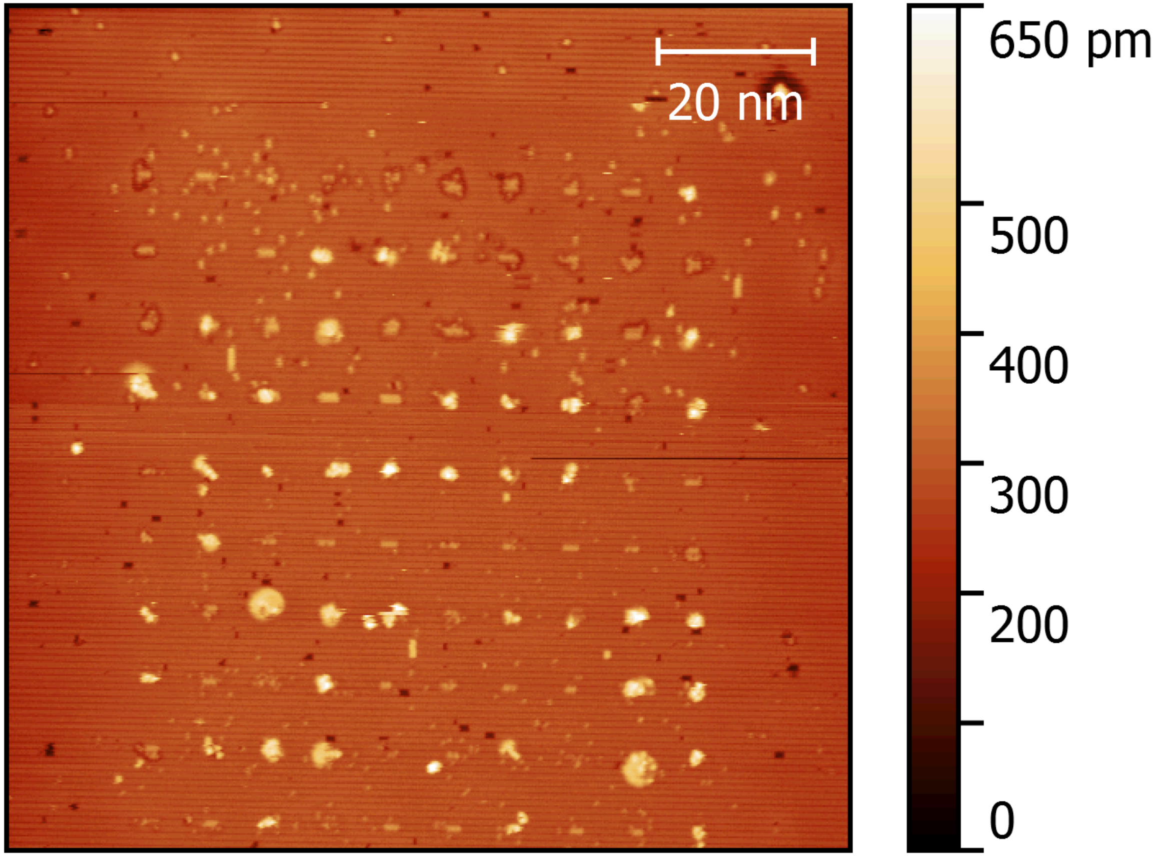
Warschkow, *J. Chem. Phys.*, 144 (2016)

Route to single P donor incorporation



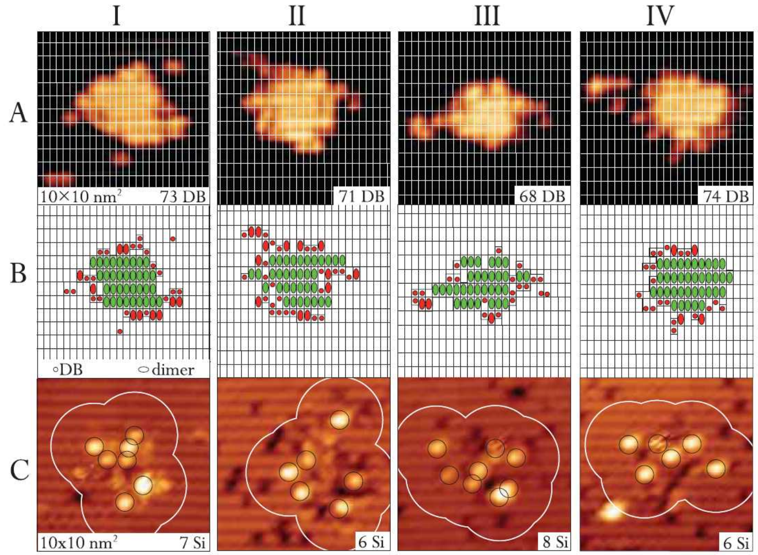
Fuechsle, *Nat. Nano.*, 7 (2012)

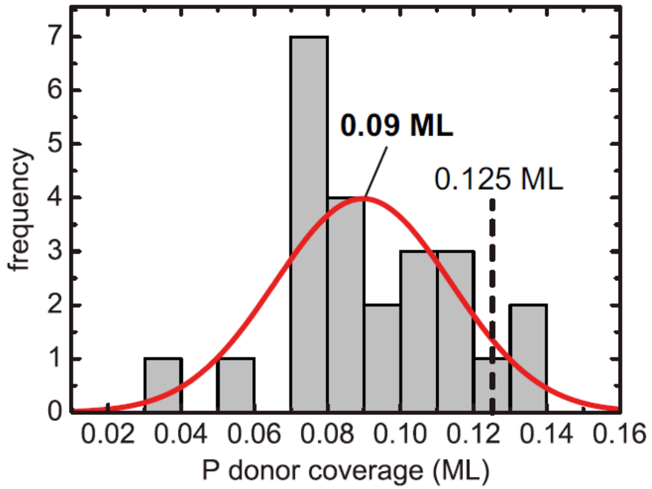
Lithographic Arrays – Tip Limitations



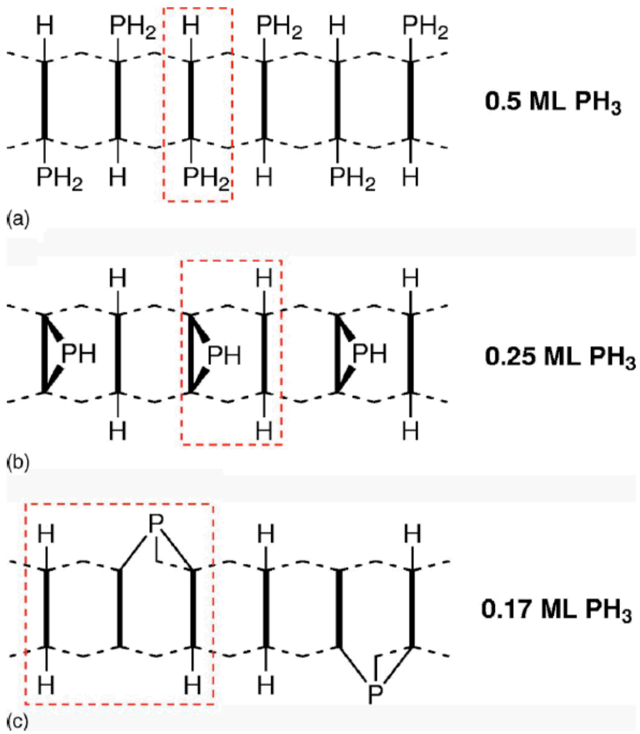
Tip limitations: drops material, apex changes leading to misalignment, apex modifications alter conditions for successful writing.

Donor Yield in Small Lithographic Boxes





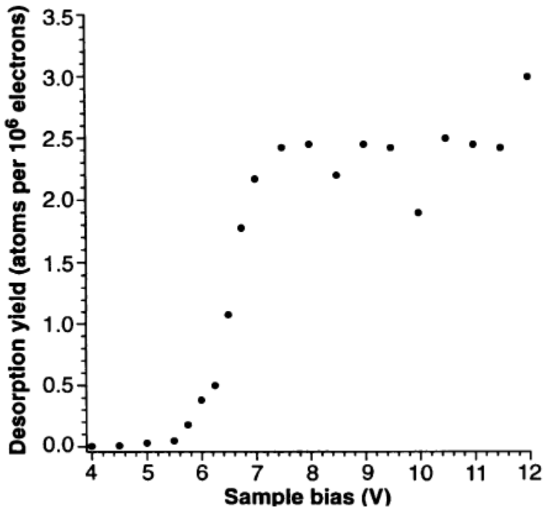
Fuechsle, *Ph.D. Dissertation* (2011)

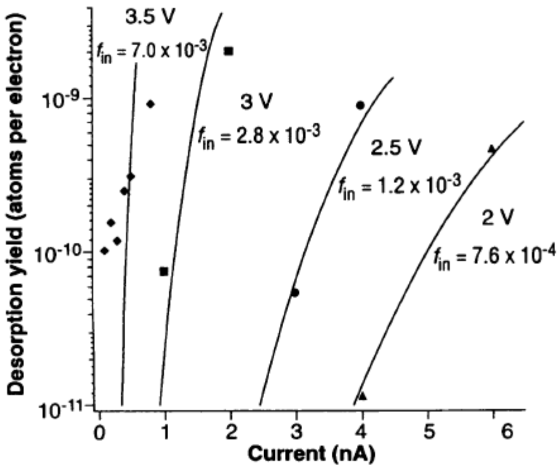


Wilson, *Phys. Rev. B*, 74 (2006)

STM Hydrogen Lithography Mechanisms

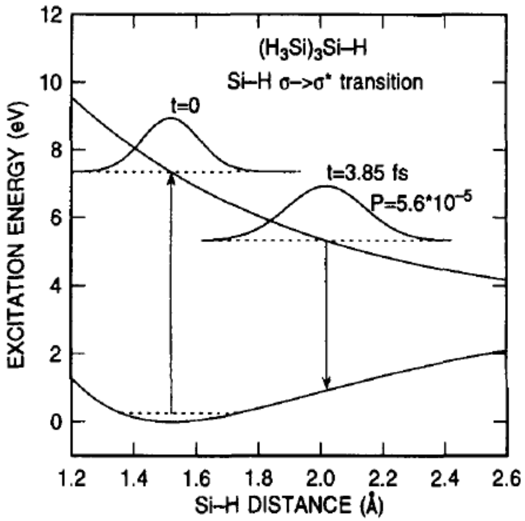
Bias/Current Dependence of H Desorption Yield





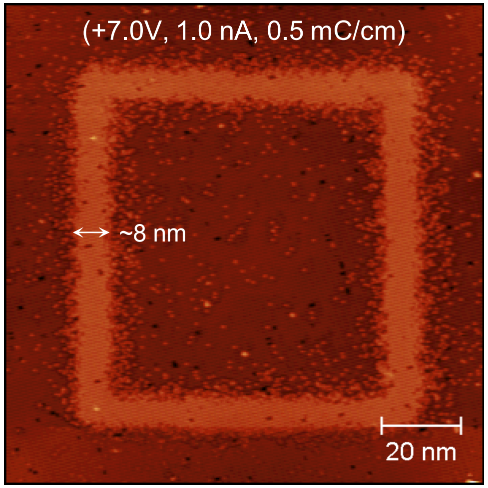
Shen, *Science*, 268 (1995)

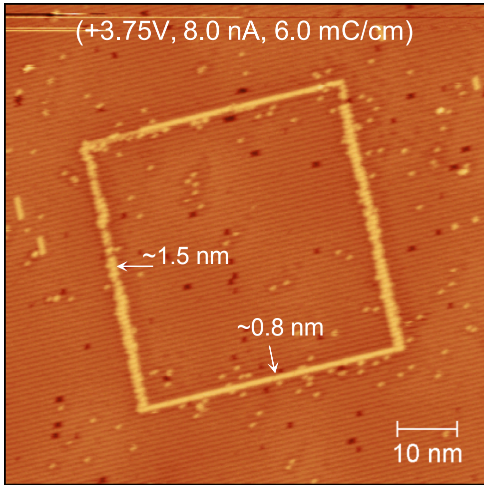
Two H Desorption Mechanisms



Avouris, *Chem. Phys. Lett.*, 257 (1996)

Two Patterning Fidelity Regimes

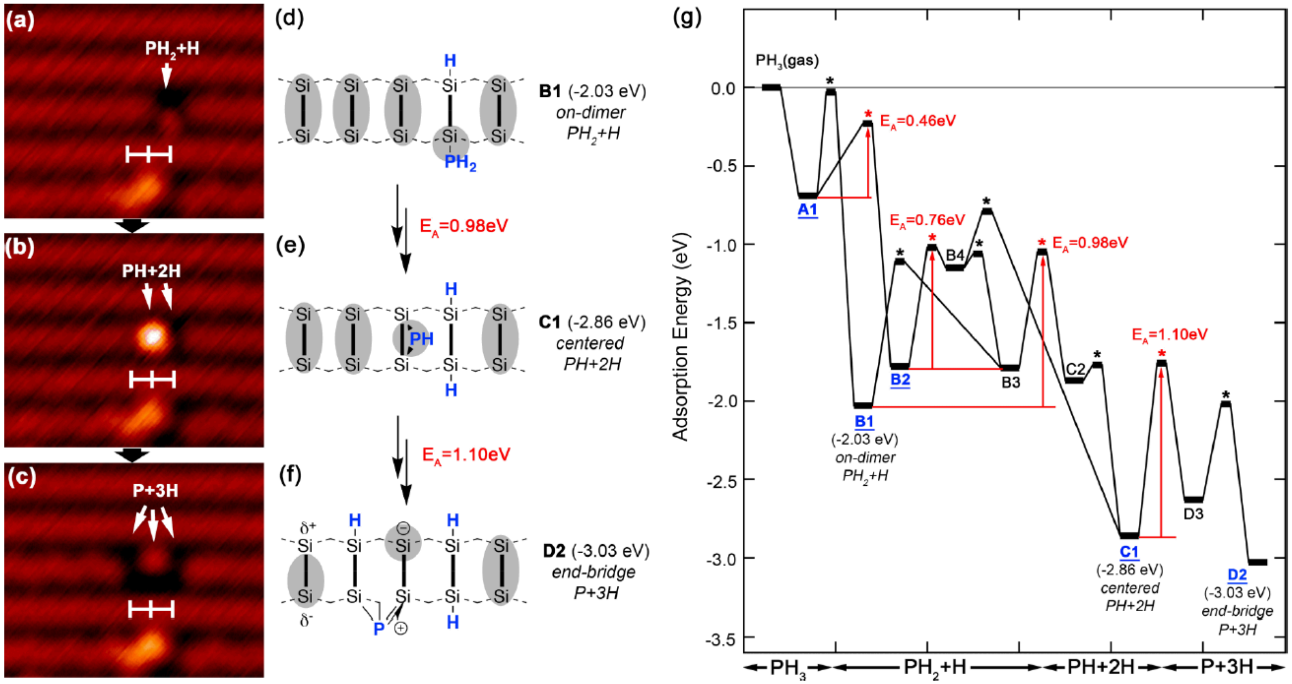




P Donor Incorporation Mechanism

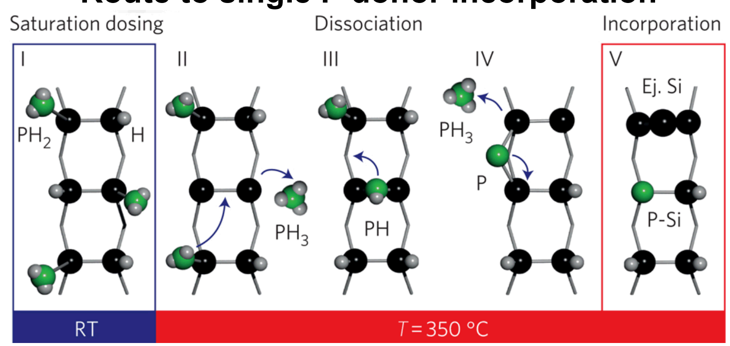
Sandia National Laboratories

Adsorption and Dissociation of PH_3 on Si(100)



Warschkow, *J. Chem. Phys.*, 144 (2016)

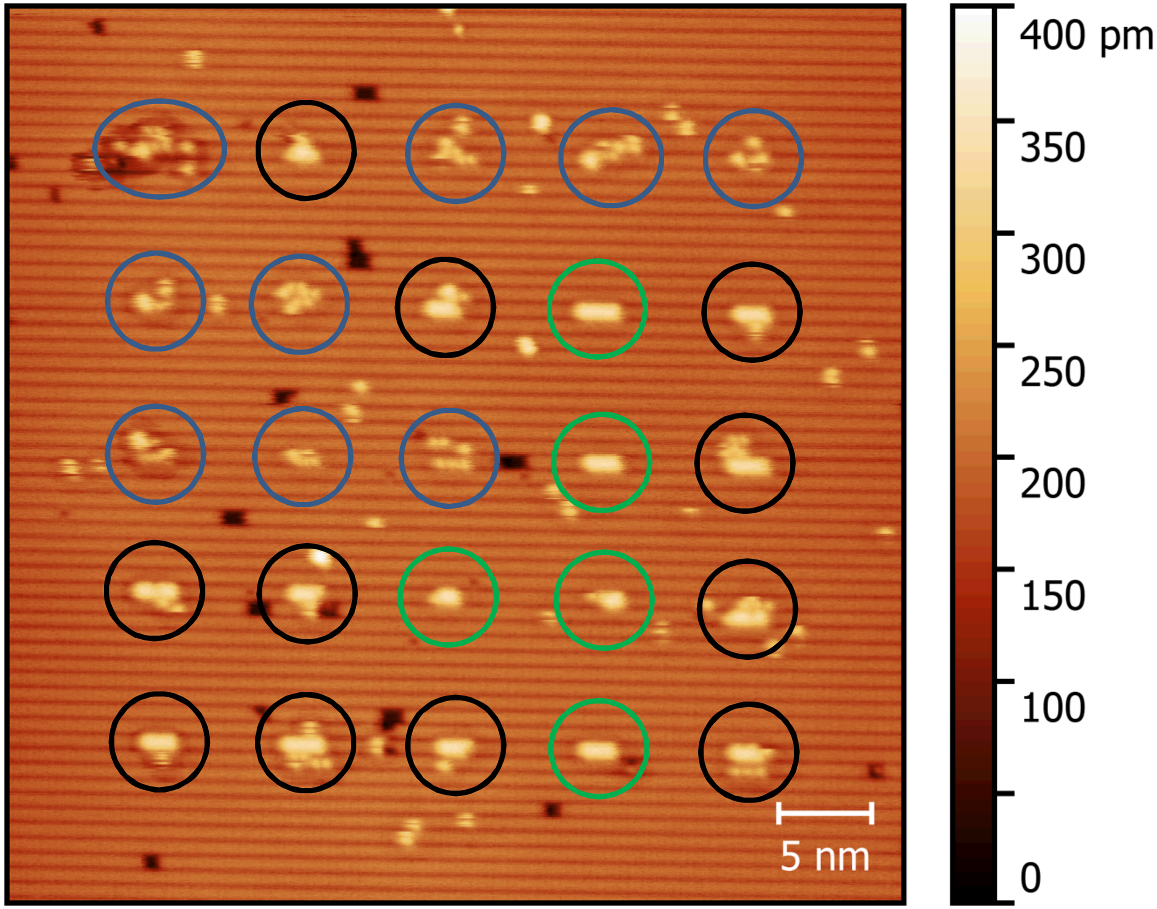
Route to single P donor incorporation

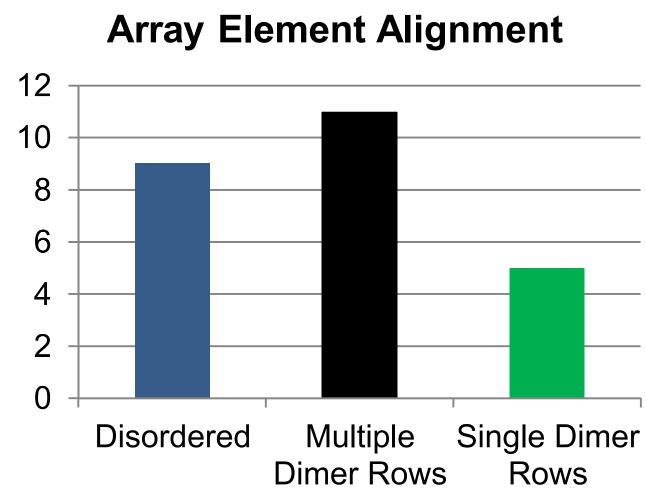


Fuechsle, *Nat. Nano.*, 7 (2012)

Lithographic Arrays – Alignment

5x5 Litho Array Litho Parameters:
(+2.75 V, 15.0 nA, 10.0 mC/cm, 15 nm/s)

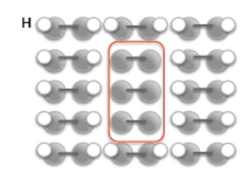




Single Dimer Row Yield: 5/25

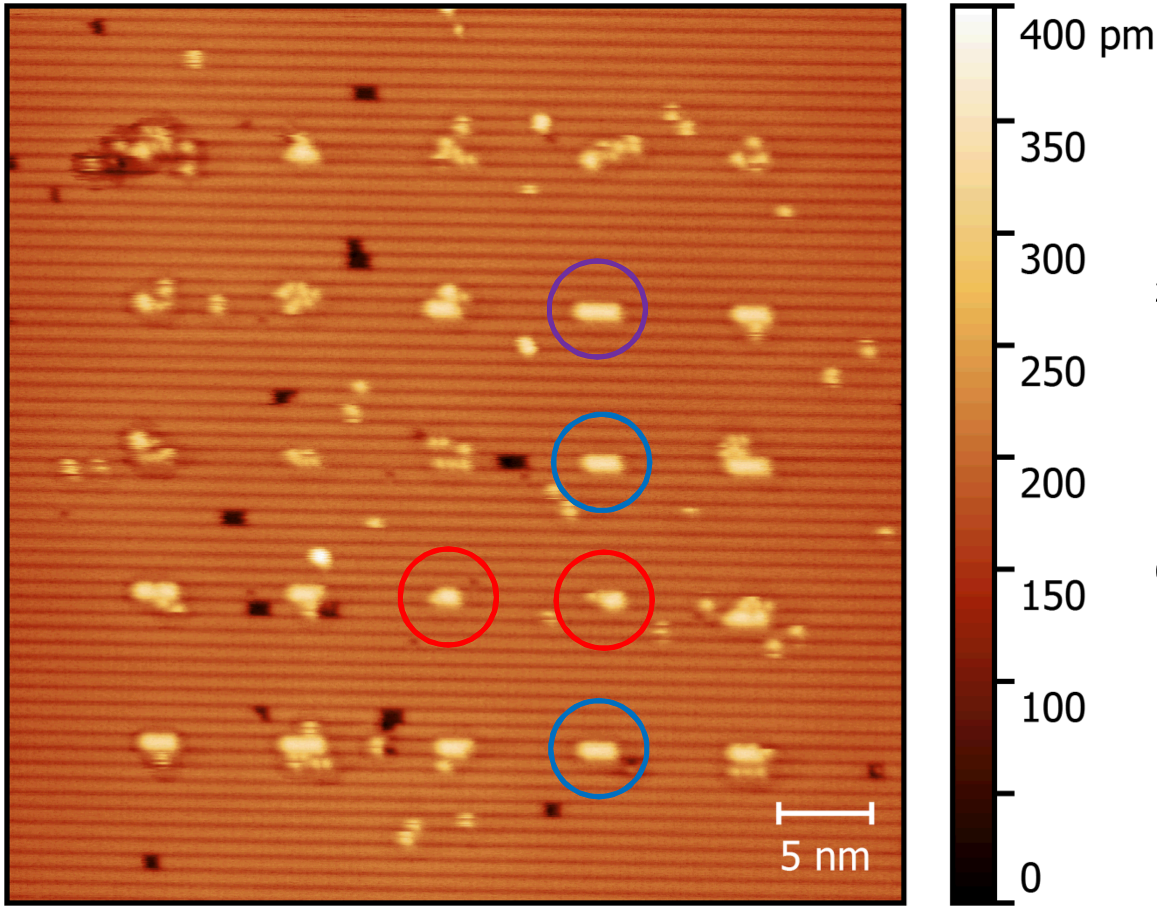
Disordered Features
Multiple Dimer Row Features
Single Dimer Row Features

Target Litho Array Element: <u>1x3 Dimers</u>

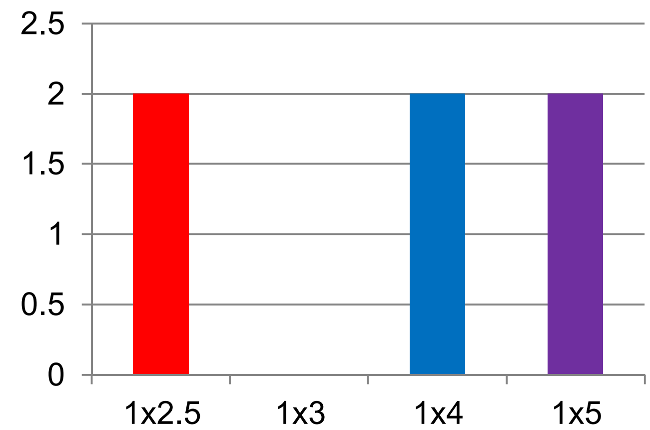


Lithographic Arrays – Pattern Length

5x5 Litho Array Litho Parameters:
(+2.75 V, 15.0 nA, 10.0 mC/cm, 15 nm/s)



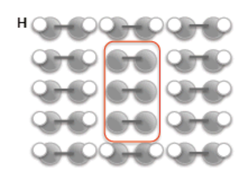
Single Dimer Row Pattern Length (Dimers)



Yield of 1x3 Dimer Patterns: 0

1x2.5 Dimers
1x3 Dimers
1x4 Dimers
1x5 Dimers

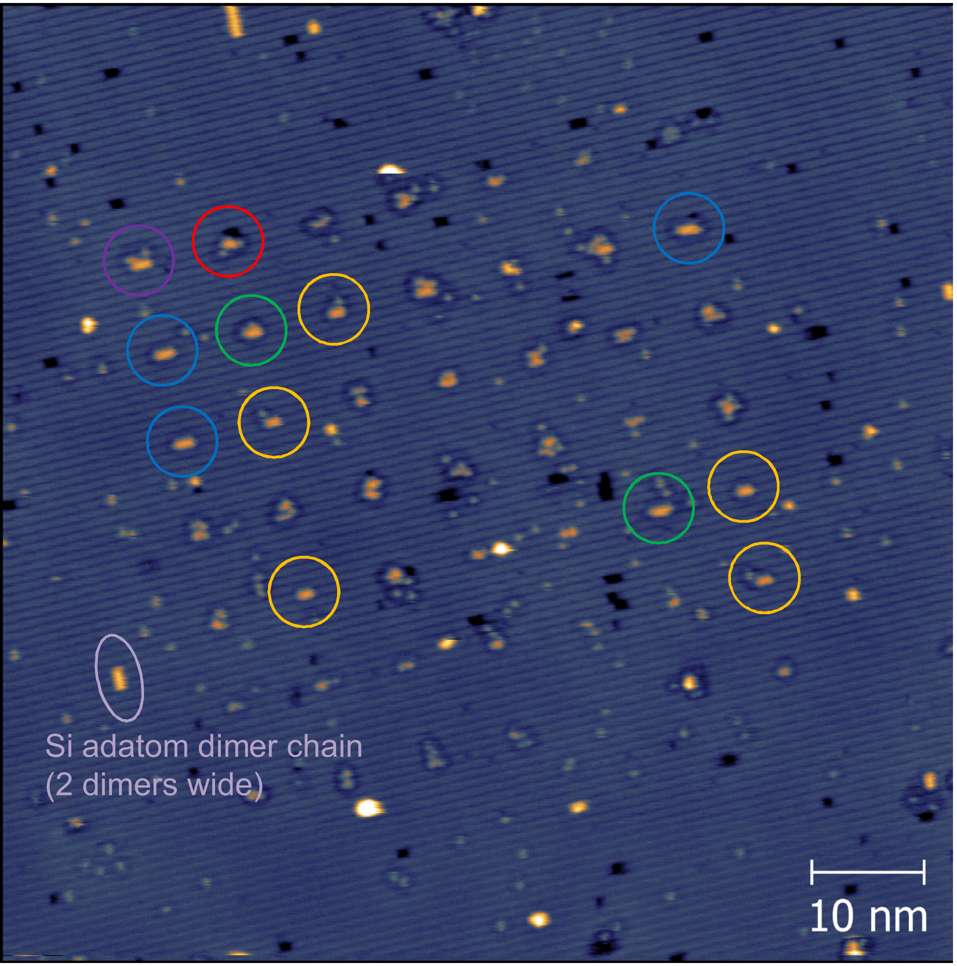
Target Litho Array Element: <u>1x3 Dimers</u>



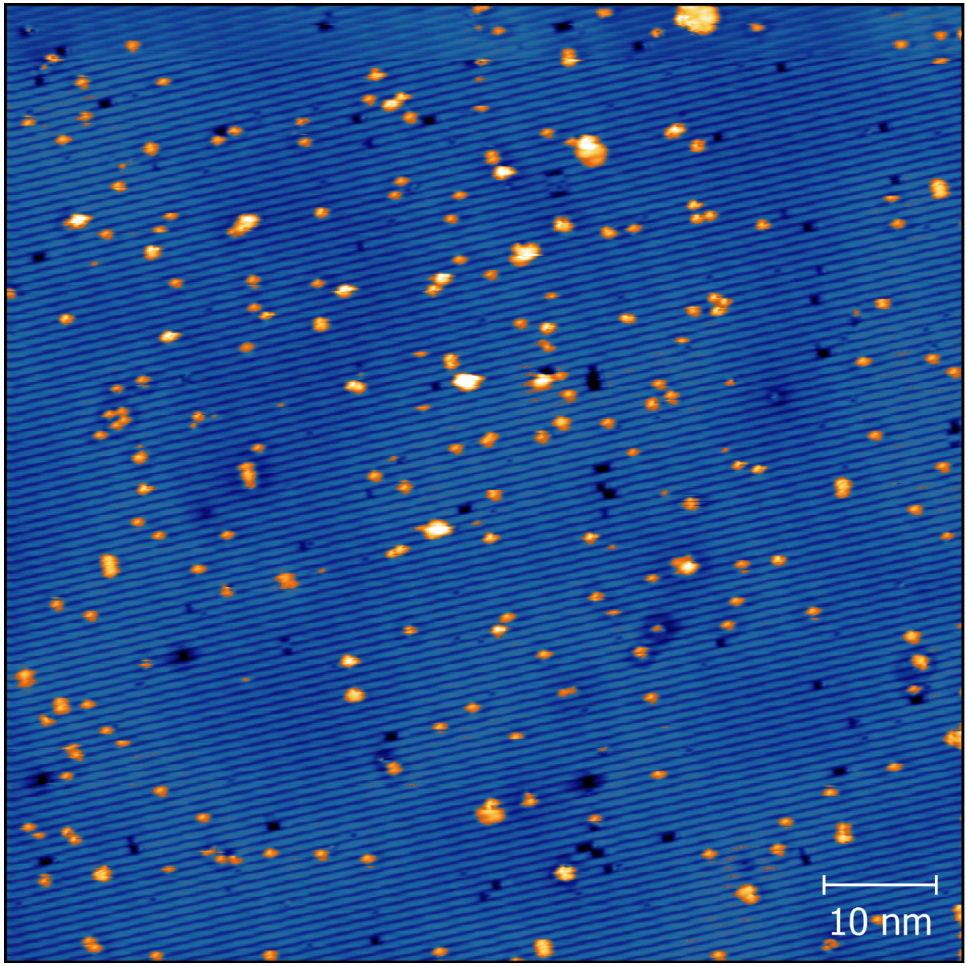
P Donor Incorporation in Lithographic Arrays

Sandia National Laboratories

7x7 Lithographic Array



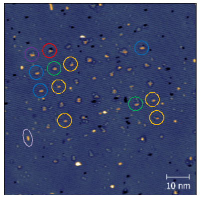
After PH_3 Dose and Incorporation



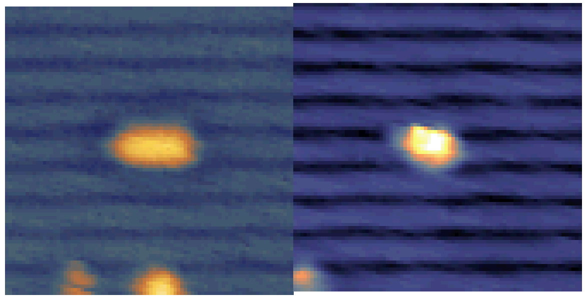
P Donor Incorporation in Lithographic Arrays

Sandia National Laboratories

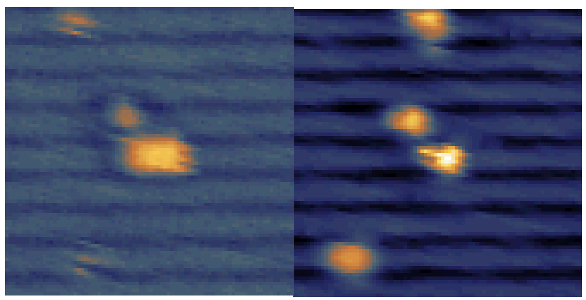
7x7 Litho Array



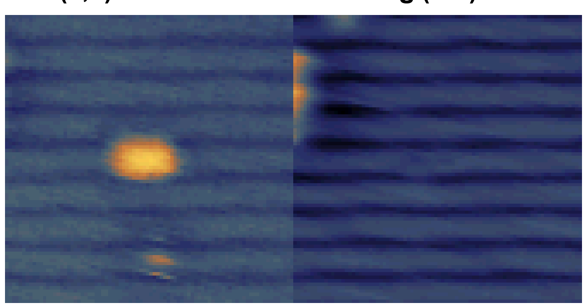
Post Litho	Post PH_3 Dose & Incorporate
Element (3,1): 1x4 Dimers	Pair of ejected Si adatoms: 2 P incorporated (fail)



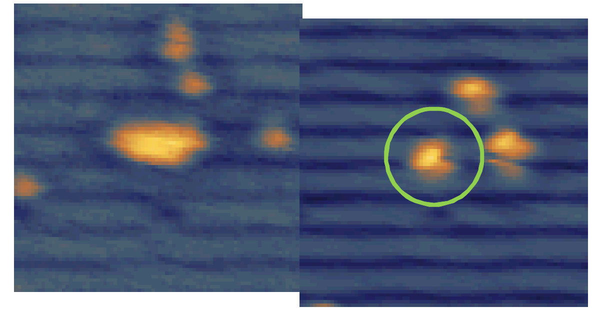
Post Litho	Post PH_3 Dose & Incorporate
Element (3,2): 1x3 Dimers	Single Ejected Si



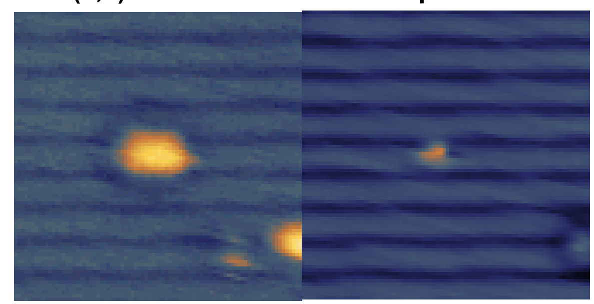
Post Litho	Post PH_3 Dose & Incorporate
Element (5,2): 1x3 Dimers	Nothing (fail)



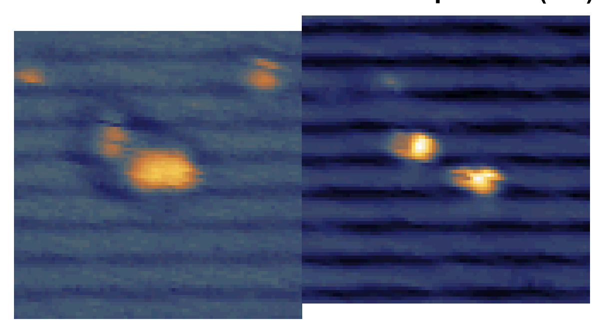
Post Litho	Post PH_3 Dose & Incorporate
Element (5,6): 1x3.5 Dimers	Single Ejected Si



Post Litho	Post PH_3 Dose & Incorporate
Element (5,7): 1x3 Dimers	Incorporated P

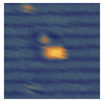


Post Litho	Post PH_3 Dose & Incorporate
Element (6,7): 1x3 Dimers	Pair of ejected Si adatoms: 2 P incorporated (fail)?



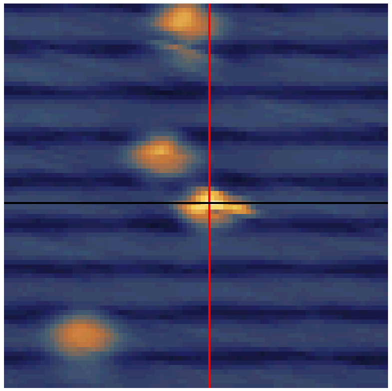
P Donor Incorporation in Lithographic Arrays

Post Litho, Pre-PH_3

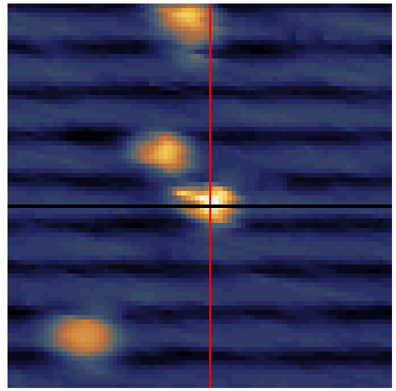


Array Element (3,2) – 1x3 dimers

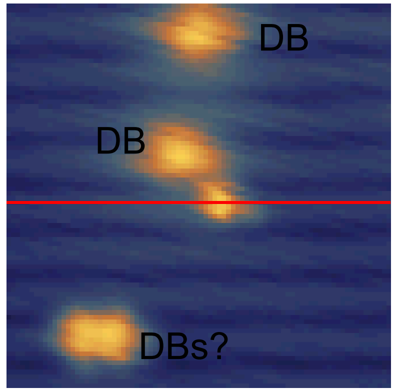
Post-PH_3 Incorporation (filled states), trace



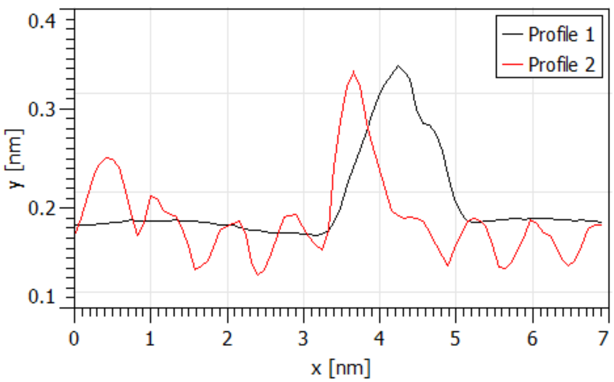
Post-PH_3 Incorporation (filled states), re-trace



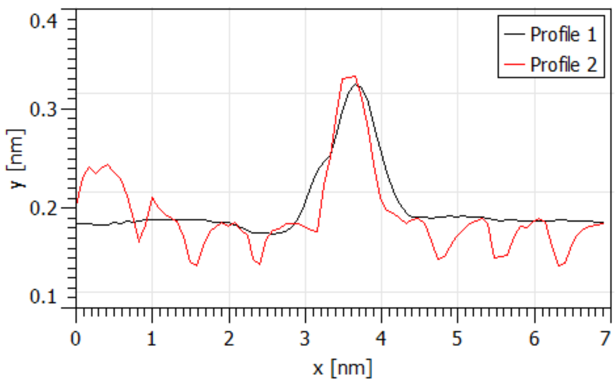
Post-PH_3 Incorporation (empty states)



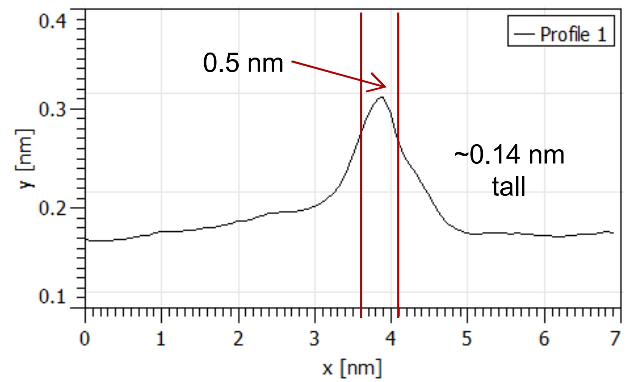
Single ejected Si atom



Along dimer row cross section:
~0.165 nm tall and ~0.67 nm wide
Across dimer row cross section:
~0.166 nm tall and ~0.39 nm wide



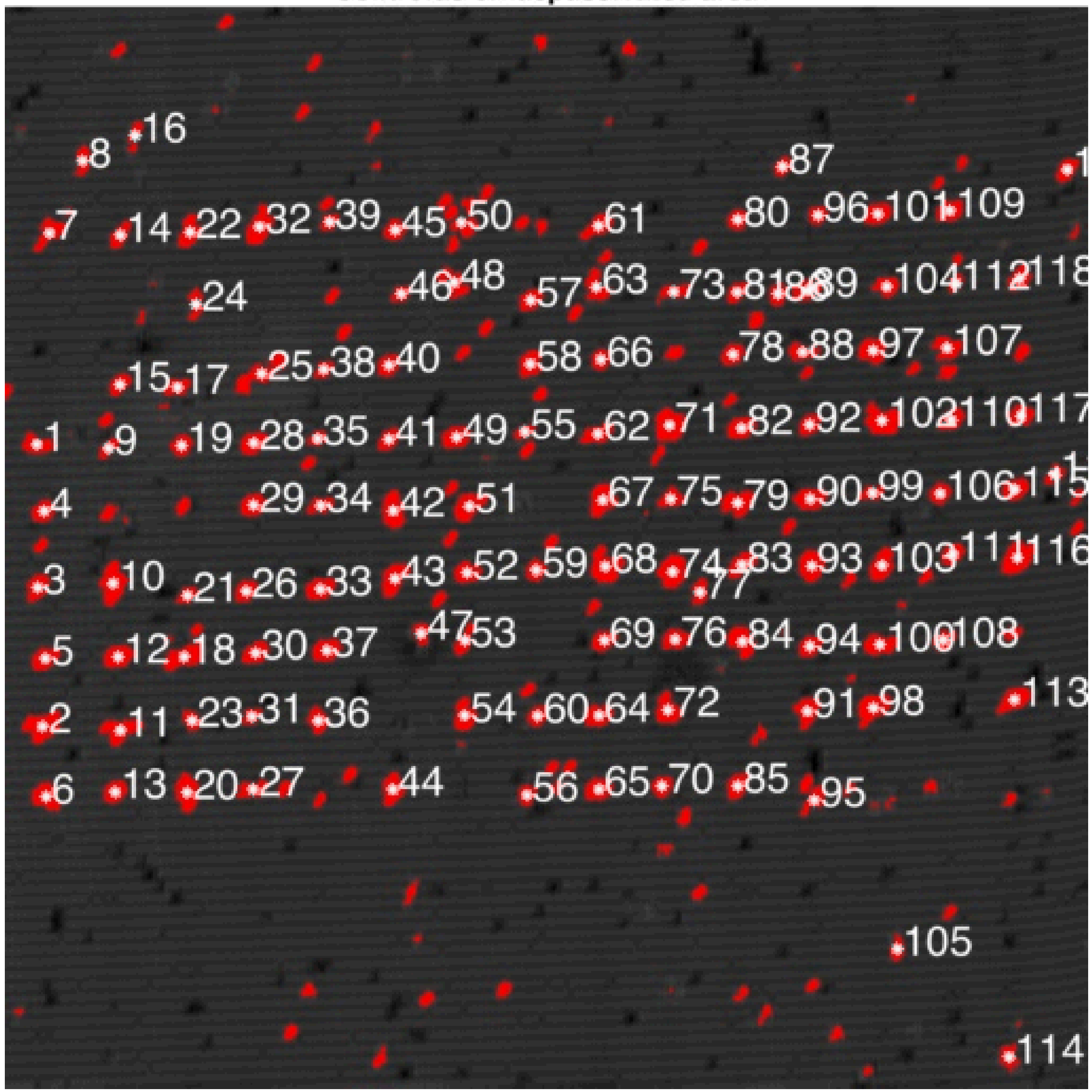
Along dimer row cross section:
~0.150 nm tall and ~0.51 nm wide
Across dimer row cross section:
~0.169 nm tall and ~0.46 nm wide



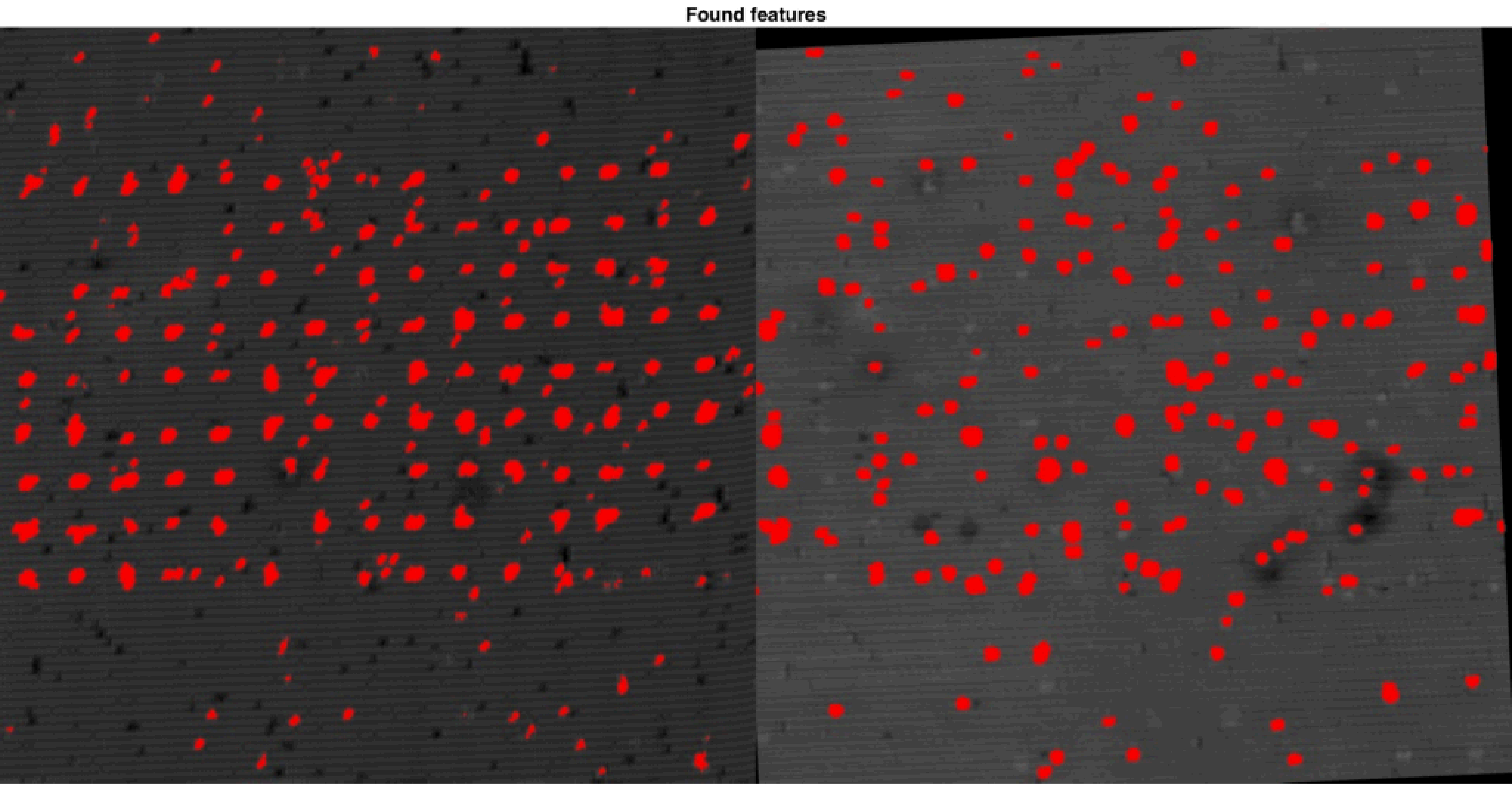
Feature Identification for Array Analysis

Sandia National Laboratories

Centroids on depassivated area

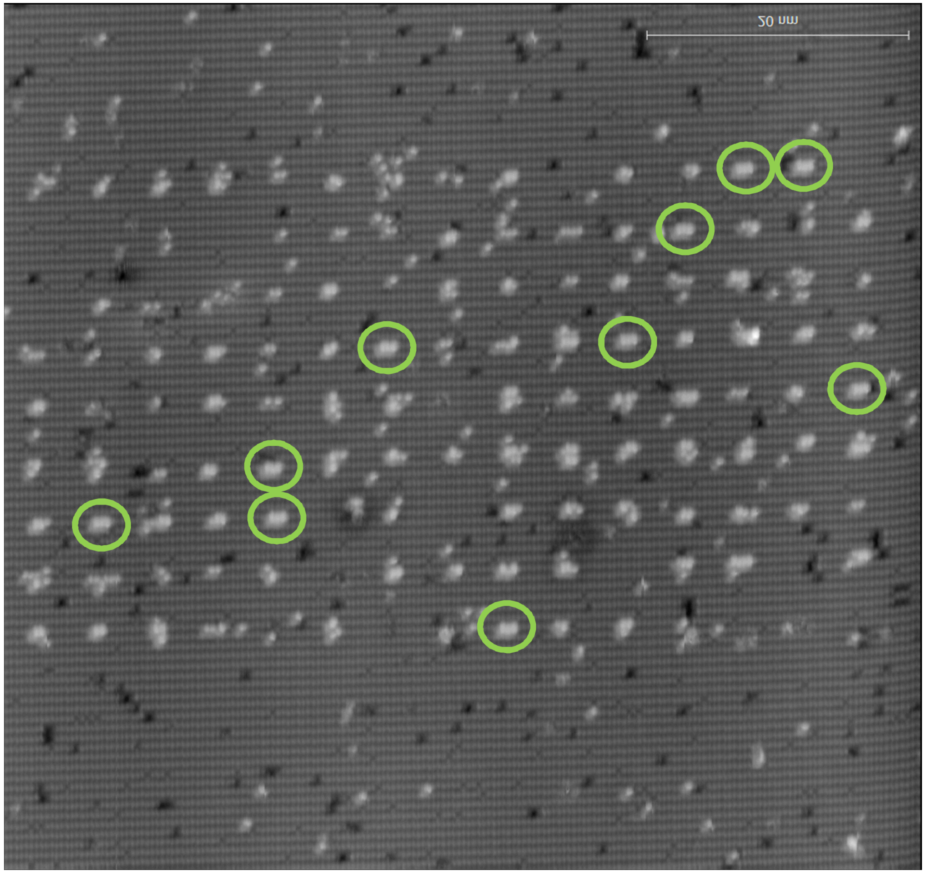


Feature Identification for Array Analysis

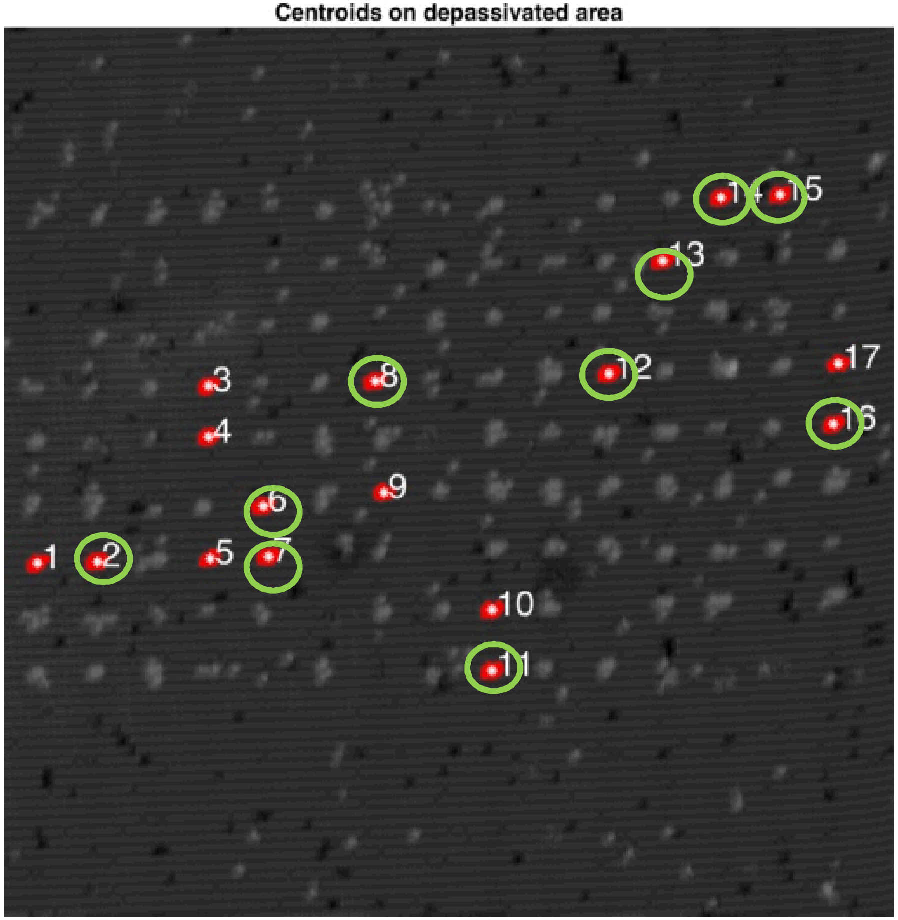


Feature Identification for Array Analysis

Now refind regions using data from successes (minor/major axis + area)



10 areas



All 10 real area / Total of 17 areas