Selective Deposition in STM Lithography-defined Patterns: transfer into 2D and 3D patterns

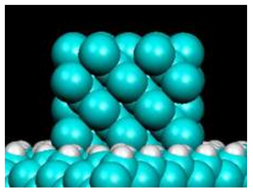
J. H. G. Owen* [a], J. Ballard [a], J. Lake [a], R. Santini [a], J. N. Randall [a] and J. R. Von Ehr [a]

[a] Zyvex Labs LLC, 1301 N. Plano Rd, Richardson, TX 75081, USA

* **jowen@zyvexlabs.com www.zyvexlabs.com**

Atomically Precise Manufacturing

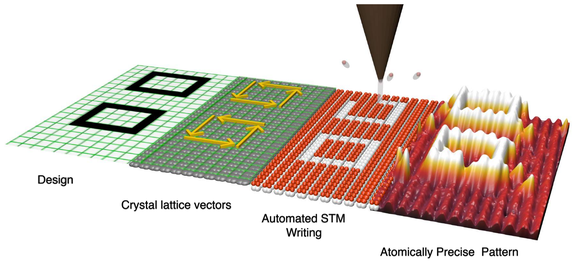
Long-term Vision

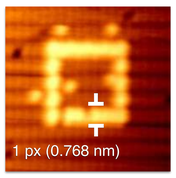


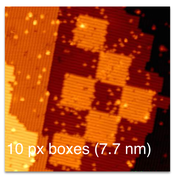
- Take dimensional precision to its limit: the crystal structure of the material.
- Top Down Control to create designed 3D structures, atom by atom.
- Atomic Precision (± 1 atom size) at first, moving to Absolute Precision in the future.

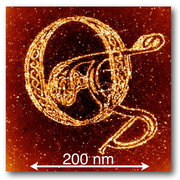
Atomically-Precise Patterning

- Atomically-precise patterns are drawn on Si(001):H using STM-based H depassivation lithography.
- We define patterns with respect to a pixel comprising 2 Si dimers on the same dimer row, giving a pixel size of 0.768 nm × 0.768 nm.
- With this pixel basis, we can define and draw arbitrary structures at the atomic scale.



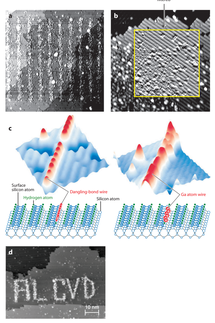






Pattern Transfer by Selective Deposition

How to transfer these atomically-precise patterns into 2D or 3D sructures?



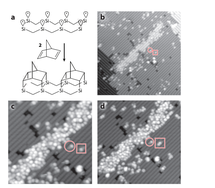
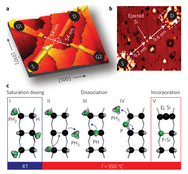


Figure 5
(a) A schematic of the binding chemistry for norbornadiene (NBE) molecules on clean silicon. (b) A line of dangling bonds patterned with the scanning tunneling microscope (STM) probe. (c) STM image of the surface following a 0.02-L dose of NBE. The box and circle highlight individual NBE molecules adsorbed to single dangling-bond sites. (d) Following a subsequent dose of NBE, the box shows the NBE molecules beginning to line up head to tail, exhibiting a form of molecular self-assembly. Figure adapted from Reference 46, with permission from Elsevier.

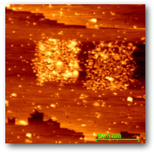
Annu. Rev. Phys. Chem. **60** 193-216 (2009)
DOI:10.1146 /annurev.physchem.040808.090314

Many attempts at metal or molecular selective adsorption.

Dopant Patterning for 2D devices



Weber *et al. Science* **335** 64-67 (2012)
DOI: 10.1126/science.1214319

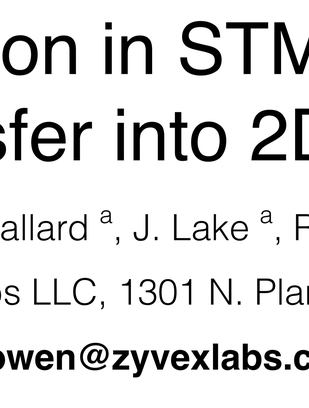


PH_3 selectively adsorbed into two patterns on Si(001):H

- Atomically-precise placement of P atoms deposited from PH_3, has been used to make P-based spin or charge qubit devices.
- We aim to develop similar processes for acceptor dopant precursors, such as diborane, or alanes.

Patterned Atomic Layer Epitaxy (P-ALE+) of Si

- During growth, the surface temperature must be less than 300°C, the onset of H atom mobility.
- Pattern the growth area.
- Move tip away to avoid shadowing of disilane.
- Expose to a saturation dose of disilane, which fills the area with SiH_x fragments, while being unreactive with the background H-terminated dimers.
- Repeat HDL to remove H from the disilane fragments, leaving the Si atoms behind, which form about ⅓ ML of islands.
- After 3 cycles of disilane exposure and tip-driven H removal, a monolayer of Si will have been deposited.
- Growth of several ML has been performed, but the surface becomes progressively rougher.

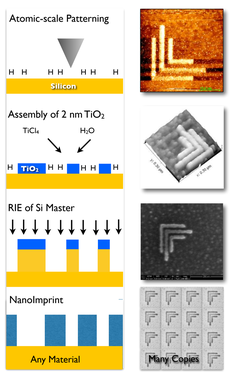


Owen *et al., J. Vac. Sci. Technol.* B **29** 06F201 (2011)

DOI: 10.1116/1.3628673

Patterned Atomic Layer Deposition of TiO_2

- Pattern the growth area using HDL.
- Move surface to ALD chamber.
- Grow using standard ALD process, with $TiCl_4$ and water as precursors.
- Etch using Reactive Ion Etching (RIE).
- Master can be used to transfer pattern into resist using NanoImprint Lithography.
- Pattern can thereby be transferred into any material.

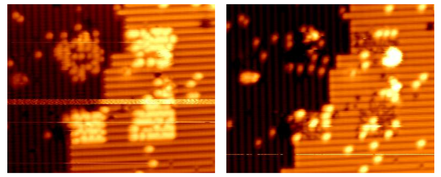


J. Vac. Sci. Technol. B **32** 03D112 (2014)

DOI:10.1116/1.4864619

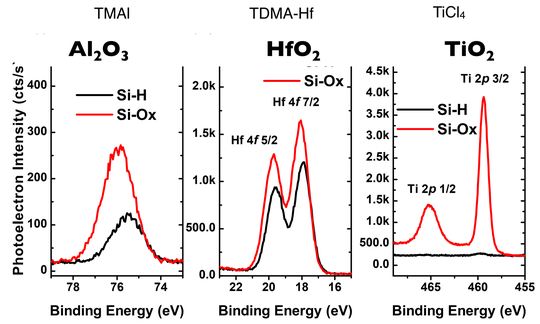
Chemistry of Selective ALD

Precursor Selectivity



- Water, as shown here, and ammonia show strongly selective adsorption into the patterned areas. This prepares the surface for the metal precursor.

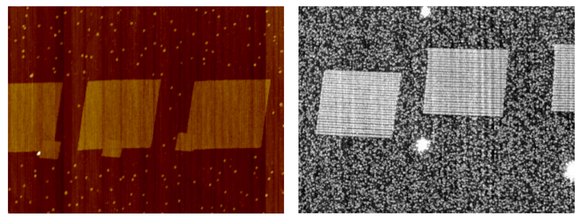
Metal Precursor Selectivity



Metal Precursor	Barrier on Si-OH	Barrier on Si-H	Selectivity
TMA	0.05 eV	1.35 eV	**1.30 eV**
$TiCl_4$	0.26 eV	1.50 eV	**1.24 eV**
TDMA-Hf	0.73 eV	1.45 eV	**0.72 eV**

- In ALD experiments, both $TiCl_4$ and TMA have shown selectivity in different dose windows, while TDMA-Hf has not.

Defect Nucleation sites for Background Growth

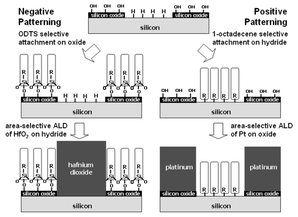


- While there is strong chemical contrast between the patterns and the ideal H-terminated surface, the passivity is limited in practice by missing H atoms, which provide nucleation sites for background growth.

Other Possible Pattern Transfer Methods

- **We are actively searching for other selective adsorption processes to broaden the range of applications of STM Lithography.**

Other resists?

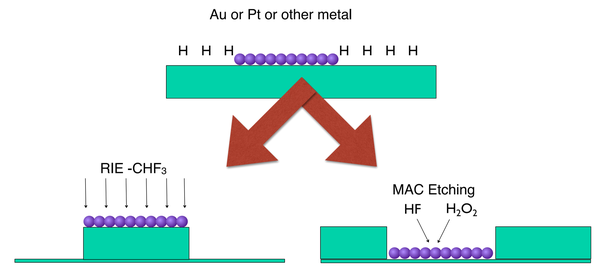


From Chen and Bent, Adv. Mater. **18**, 1086–1090 (2006)

DOI: 10.1002/adma.200502470

- Hydrocarbons have a strong physisorbing interaction with the H background. By filling the pattern with OH or NH_2 species, we may be able to use chemical contrast to transfer the STM pattern into more robust resist molecules.
- Stability of the the H and NH_2 groups in air are an issue, however.

Noble Metal Deposition?



Conclusions and Further Work

- STM Lithography is an attractive way to make atomically-precise patterns
- Broadly applicable pattern transfer processes remain a challenge.
- Passivity of background H termination is limited by defects, and limited lifetime in ambient conditions.
- Development of a method to transfer the H resist into a more robust material would be highly beneficial for this technique
- Development of a method to pattern a noble metal such as Su, Pt etc. would open a wide range of possible applications.
- Encyclopedia of Interfacial Chemistry: Surface Science and Electrochemistry article in proof stage: DOI: 10.1016/B978-0-12-409547-2.13149-X

Acknowledgements

- This work has been supported by the Defense Advanced Research Project Agency (DARPA) under Contract N66001-08-C-2040, and the 'Atoms to Product' Program administered by AFRL Contract FA8650-15-C-7542. Some of this work was supported by the Texas Emerging Technology Fund of the State of Texas for the Atomically Precise Manufacturing Consortium.