This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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2020 VIRTUAL MRS® SPRING/FALL MEETING & EXHIBIT

November 27 – December 4, 2020

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2020 VIRTUAL MRS® SPRING/FALL
MEETING & EXHIBIT

Triethyl Aluminium—A Precursor for Atomically-Precise Acceptor Dopant Placement ?

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SINGLE-DOPANT PLACEMENT

- During Atomic Precision Advanced Manufacturing, (APAM), an STM tip is used to remove H atoms from the Si(001) surface, creating reactive patterns.
- PH_3 adsorbs into these patterns selectively, allowing the atomically-precise placement of donor dopants, to create atomic-scale devices.

- We want to be able to make bipolar devices, including acceptor dopants (B, Al etc.).
- However, direct phosphine analogues (alanes) are not stable at room temperature.
- The most common CVD precursors are alkyls,
- e.g. tri-methyl Al (TMAl), tri-ethyl Al (TEAl).

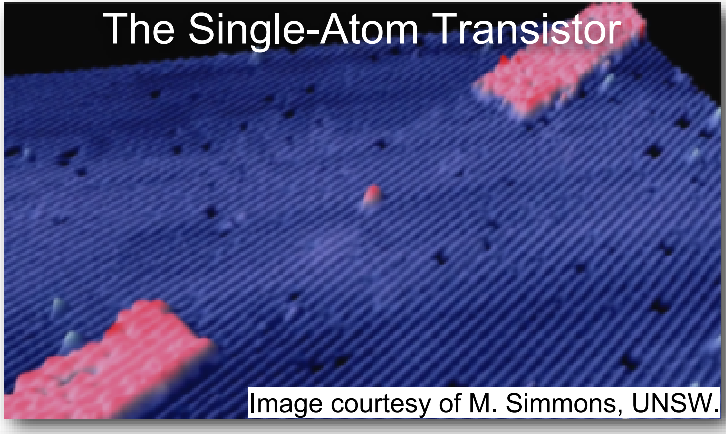
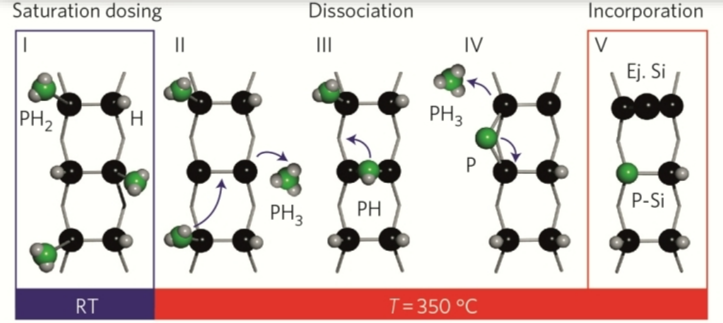
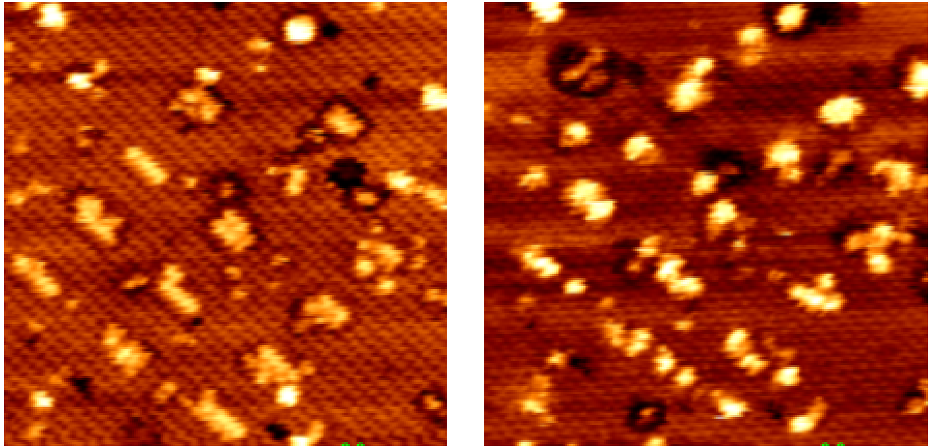

The Single-Atom Transistor

Image courtesy of M. Simmons, UNSW.

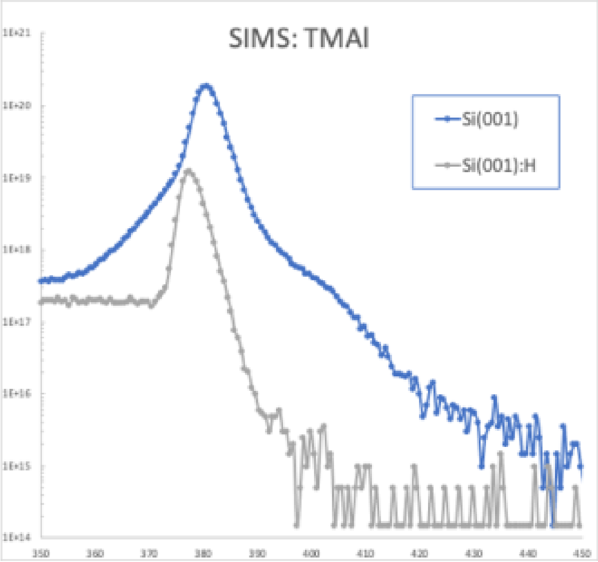
Fuechsle *et al.* *Nat Nano* **7** 242-246 (2012)
DOI: [10.1038/nnano.2012.21](https://doi.org/10.1038/nnano.2012.21)



TRIMETHYL AL SELECTIVITY TESTS

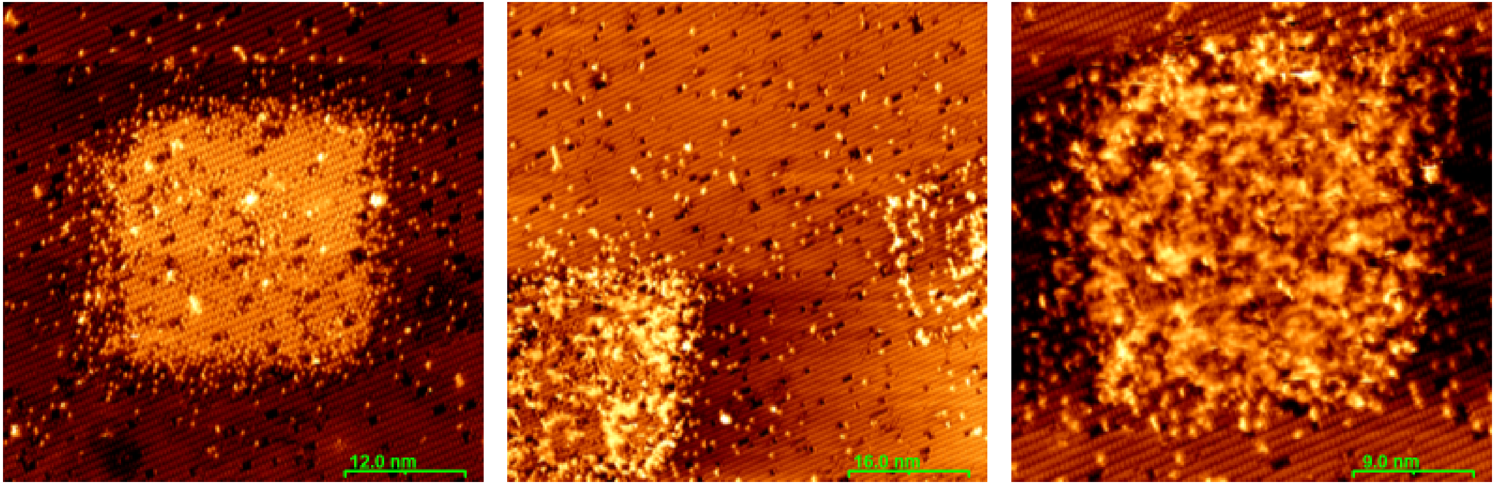


Before and after dosing 20 L TMAl into array of small patterns.



- We found TMAl to be selective (20:1), but was expected to lead to significant carbon incorporation.
- For TEAl, there is a route to carbon removal, desorption of ethylene from Si(001).

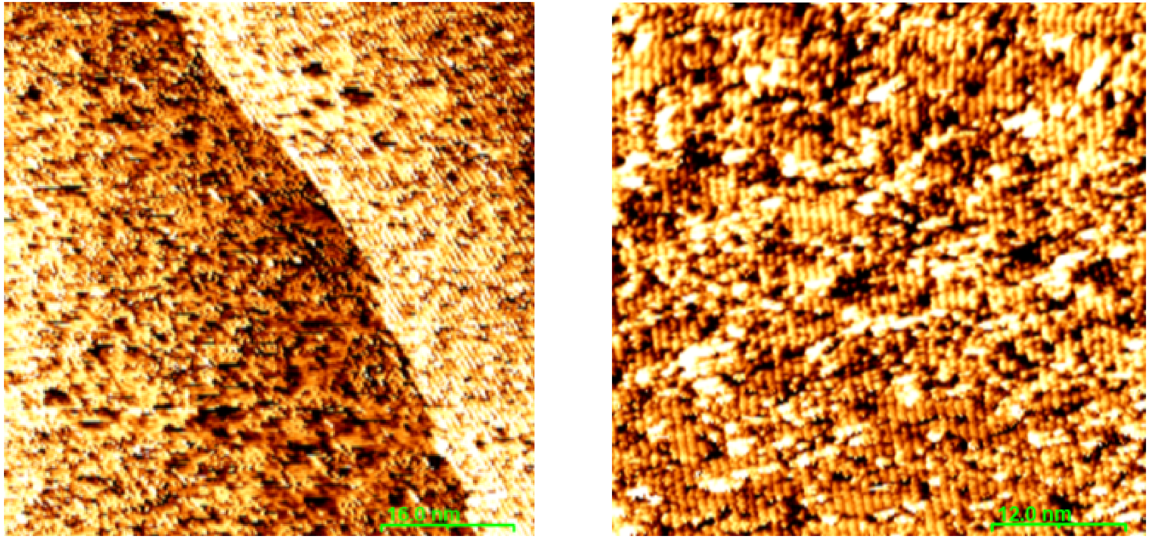
TRIETHYL AL SELECTIVITY TESTS



Before, after dosing 15 L TEAL into patterns.

- Dosing TEAl into surface patterns leads to a sub-saturation coverage of the patterned area, lower than that found with TMAl.
- Over time, the patterns fill in with more molecules, even after chamber pressure has recovered. Fresh patterns written later also fill in with molecules over time.
- -> Mobile physisorbed precursor molecules on H-terminated surface.

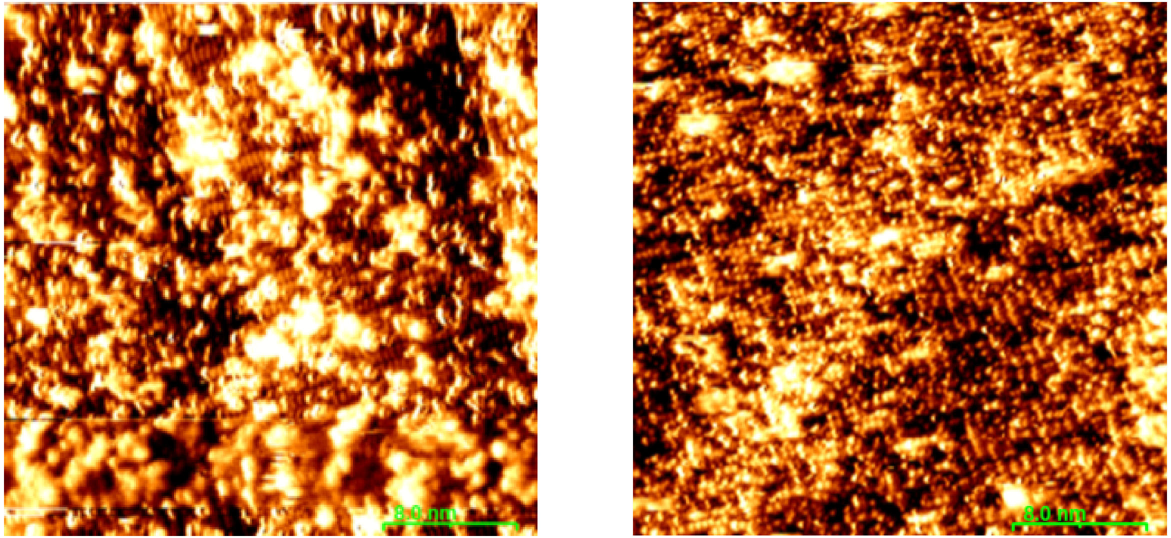
ROOM TEMPERATURE ADSORPTION



After dosing 135 L TEAl onto clean surface, then anneal 4 mins at 380°C.

- Dosing TEAl at room temperature on the clean surface does not lead to saturation adsorption.
- After an incorporation anneal, the clean surface is mostly recovered.

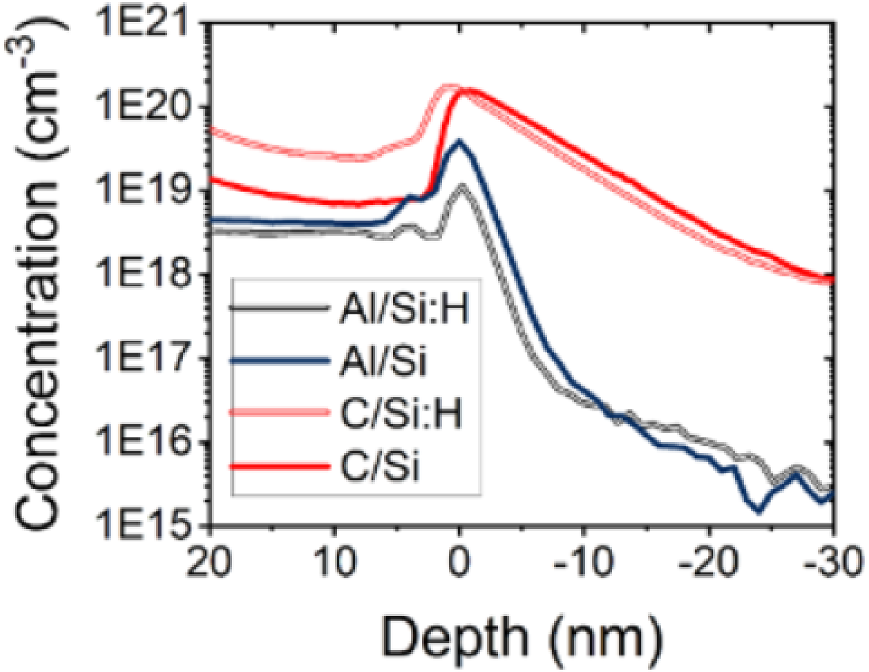
ELEVATED TEMPERATURE ADSORPTION



After dosing 100 L TEAl onto clean surface, then anneal 2 mins at 380°C.

- Adsorption at elevated temperature gives much higher adsorption coverage.
- Anneals after adsorption leads to a high density of dots, unlike the room temperature adsorption case.

TEAL DELTA LAYER PROPERTIES

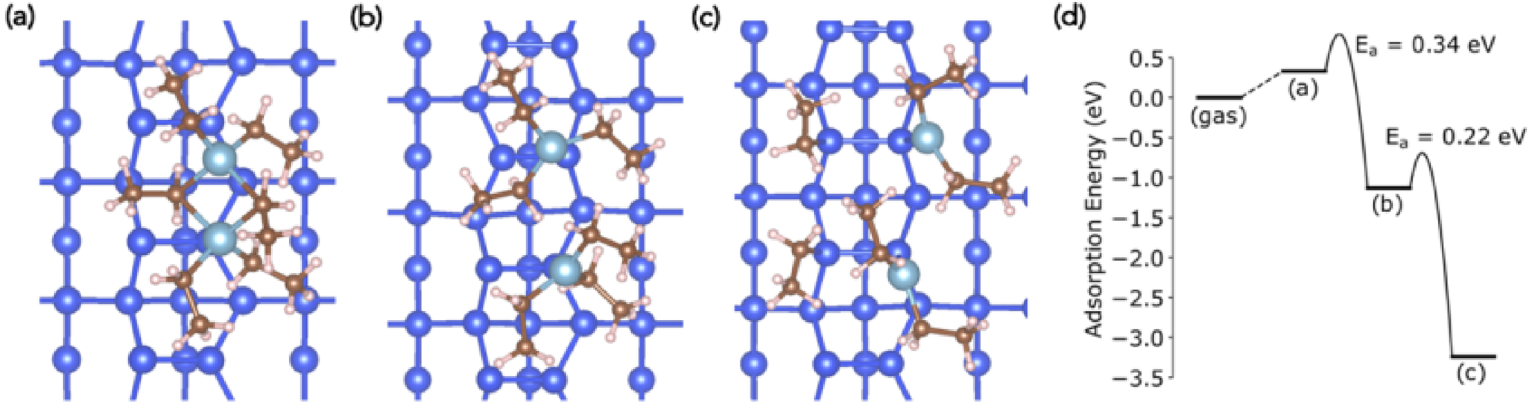


SIMS data for delta layers on clean / H-terminated surfaces.

Selectivity only 3:1.
Carbon still higher than Al.

- Using 270°C process, anneal to 380°C, and then burial in 20 nm of Si.
- SIMS data shows poor selectivity, and high carbon levels.

DFT OF TEAL DIMER ADSORPTION



DFT: Adsorption of TEAl dimer

	Adsorption energy /eV	Selectivity
TMAl / Si	-1.22 eV	20:1 (300 K adsorption)
TMAl/ H:Si	-0.01 eV	
TEAl/Si	+0.33 eV	3:1 (550 K adsorption)
TEAL/H:Si	-0.07 eV	

CONCLUSIONS

- TMAl is selective (20:1), but results in significant carbon contamination.
- TEAl dimers are not selective at room temperature, as they have a better adsorption energy on H-terminated Si(001) than clean Si(001).
- Elevated-temperature adsorption breaks the TEAl dimers, but the selectivity is still weak, ~ 3:1.
- Van der Waals interactions between the ethyl groups and the surface H leads to a population of mobile physisorbed molecules, so that patterns fill over time, as observed.
- Overall, alkyl-metal precursors are not likely to be suitable for STM-Lithography-defined patterns, due to the ligands' interactions with the H-terminated background.
- Hydride or halide precursors, e.g. $TiCl_4$, have shown strong selectivity and are likely to be preferred.
- We have therefore shifted to experiments with in-situ generation of alanes, and halide precursors, BCl_3 and $AlCl_3$.

Al-alkyls as acceptor dopant precursors for atomic-scale devices,

J.H.G. Owen et al. J. Vac. Sci. Technol. (In preparation)