Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides

Peter Sutter (psutter@bnl.gov)
Brookhaven National Laboratory
Upton, NY 11973

Brookhaven-Rutgers BES Hydrogen Team

BNL: P. Sutter, J. Muckerman
E. Sutter, J. Graetz, J. Reilly, J. Wegrzyn,
E. Muller, J.I. Flege, S. Chaudhuri.

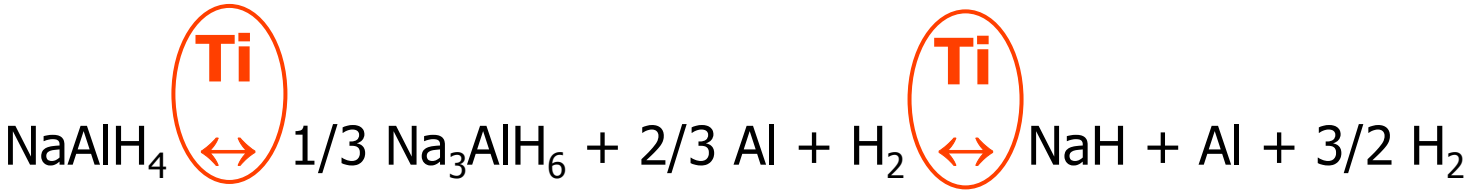
Rutgers University: Y. Chabal, J.F. Veyan.

Outline

Atomistic Transport Mechanisms in Reversible Complex Metal Hydrides

1) Introduction: Objectives & Approach
2) Examples of Activities & Findings
4) Future Plans
5) User Facilities at BNL

Doped Sodium Alanate - Key Issues



I. Fundamental questions: doping ⇔ reversible H-storage?

Q1: Role of Ti catalyst in H_2 dissociation?

Q2: Primary carrier(s) of mass transport?

Q3: Fundamental kinetic factors governing reaction rates?

II. Enhancing kinetics in other hydride systems?

Q4: Effects of substitution in mixed metal hydrides?
Re-hydrogenation of bulk alane?

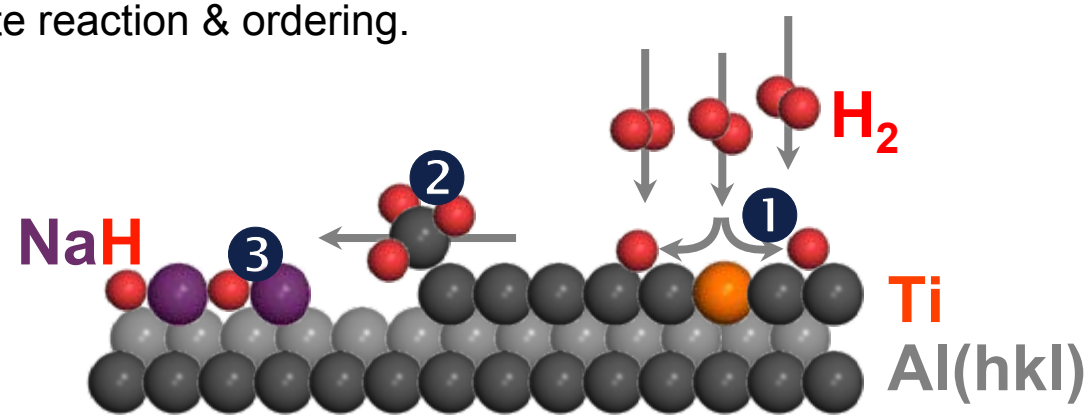
Surface Studies of Re-Hydrogenation Reaction

$$NaAlH_4 \xrightarrow{Ti} 1/3\ Na_3AlH_6 + 2/3\ Al + H_2 \xrightarrow{Ti} NaH + Al + 3/2\ H_2$$

Elementary reaction steps (at surfaces)

1. Ti catalyzed H_2 dissociation on depleted material (Al)
2. Formation of mobile species & mass transport.
3. Solid state reaction & ordering.

} Relevant to new hydrides **(Alane)**



- Model system for **atomic-level surface studies.**
- Unprecedented level of **interaction with theory.**

Research Team

Nanoscale surface imaging
[P. Sutter, BNL]

Scanning tunneling microscopy
- *atomic scale* structure.

Low-energy electron microscopy
- surface *dynamics* & mass transport.

Ab-initio theory & modeling
[J.T. Muckerman, BNL]

Density functional theory
- *atomic scale* structure & energetics.

Ab-initio molecular dynamics
- surface *dynamics*.

Quantitative spectroscopy
[Y.J. Chabal, Rutgers]

FT-infrared reflection spectroscopy
- hydrogen containing *adsorbates*.
- surface *dynamics* & mass transport.

Synchrotron & TEM techniques
[J. Graetz, E. Sutter, BNL]

XRD, EXAFS
- bulk synthesis, structure, bonding.

Analytical electron microscopy
- nanoscale structure & composition.

Activities & Findings

Significant findings to date:

1) Ti-catalyzed H_2 dissociation:

- Local Ti environment similar to $TiAl_3$ with split Al shell at ~2.8 Å (EXAFS).
- Ti has reduced coordination - near-surface sites.
- Ti atom pair complexes on Al(001) surfaces that spontaneously dissociate H_2 (DFT).
- Key feature: nodal plane of surface/H_2 HOMO midway between Ti atoms.
- Dissociated H-atoms cannot diffuse to all-Al site on flat Al(001).
- Spectroscopic STM: Ti resides in near-surface sites & interacts with H_2.

2) Formation of mobile species (surface alanes):

- Bulk materials: stoichiometric mixtures of NaH & AlH_3 react to $NaAlH_4$ (w/o Ti!).
- Atomic-H on Al: clear IR signatures of ad-Al-H, AlH_3 & higher oligomers.
- Atomic-H on Al: step-etching & alane evolution.
- High Ti concentrations: alane formation inhibited $\rightarrow$ inactivation of Ti dopant.

3) Bulk materials:

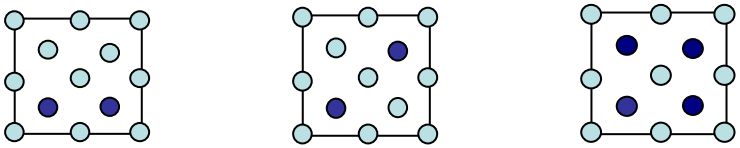
- "Elpasolite" mixed alkali alanates: K_2LiAlH_6, K_2NaAlH_6 reversible without Ti.
- No cation mixing on the same site: No tuning of thermodynamics by substitution.

1) Ti-Catalyzed H_2 Dissociation - Predictions

Ti:Al complexes on Al(001): H_2 dissociation

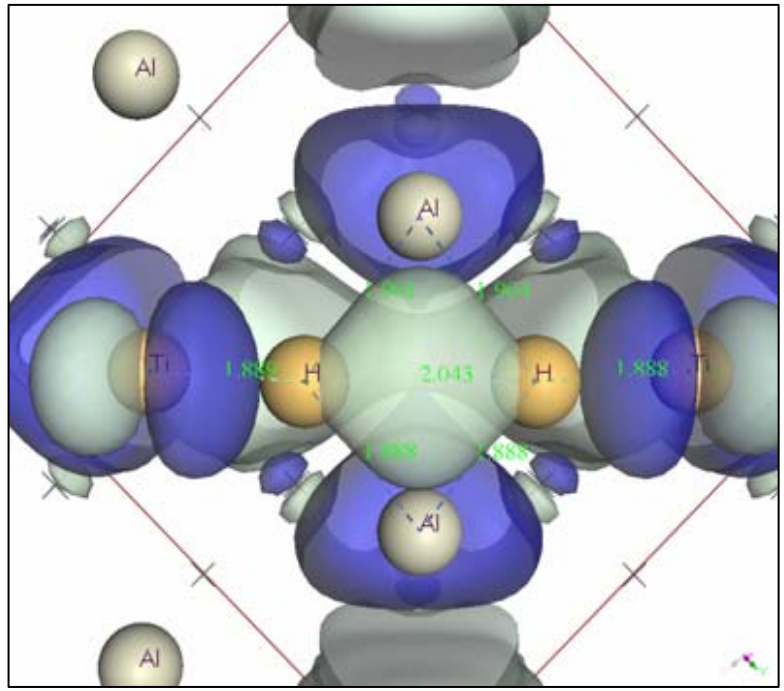
(Density functional theory)

Unit cell
(top view)



Property	Model 3	Model 4	Model 4s	Model 8
Ti Coverage	0.25 ML	0.25 ML	0.25 ML	0.5 ML
Site ΔG_f^* (eV)	3.13	2.08	1.65	1.04
E_a (eV)	0.89	**0.00**	**0.26**	1.62
Site $\Delta G_f + E_a$	4.02	2.08	1.91	2.66

*Reference state: Stable (001) surface of $TiAl_3$ alloy.



Incoming H_2 σ^* receives electron density from Ti d-orbitals.

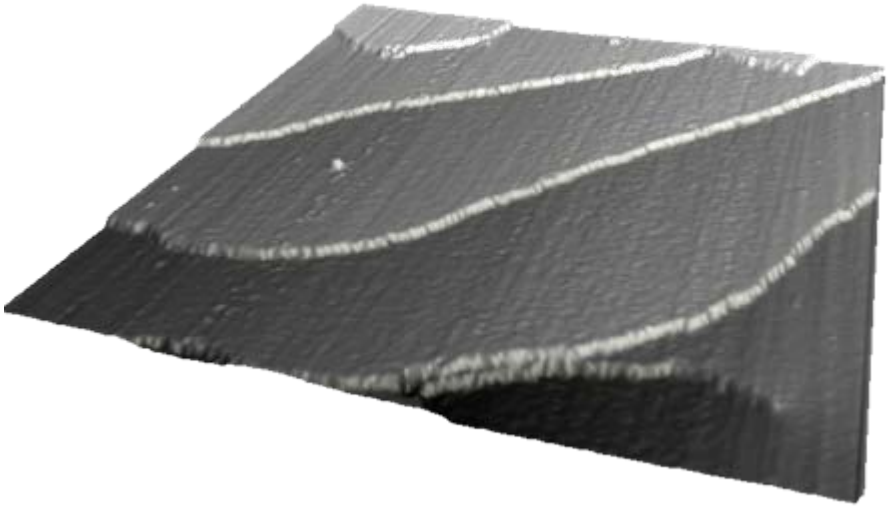
Active sites: nodal symmetry of surface/H_2 HOMO.
Other model sites: large activation barriers.

J. Phys. Chem. B 109, 6952 (2005).

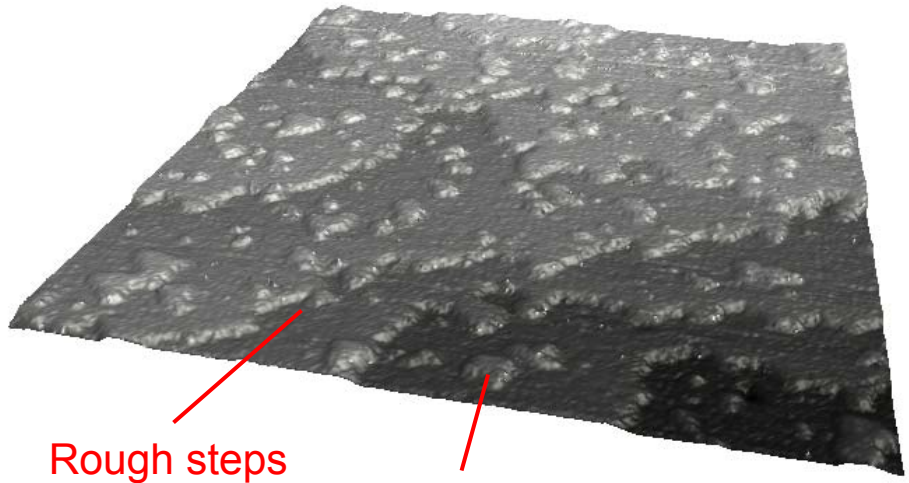
Ti/Al(111) Model System

Ti deposition on Al(111) - STM

Clean Al(111)



0.25 ML Ti/Al(111)



Ti distribution?

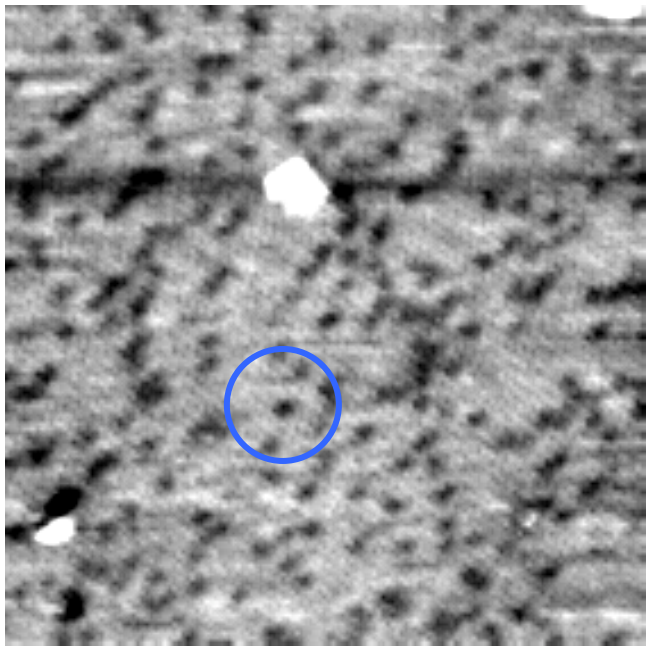
- In nucleated islands?
- Uniformly embedded?
- At surface?
- In sub-surface layers?

FOV: 80 nm.
Ti/Al(111) deposited at 400 K.

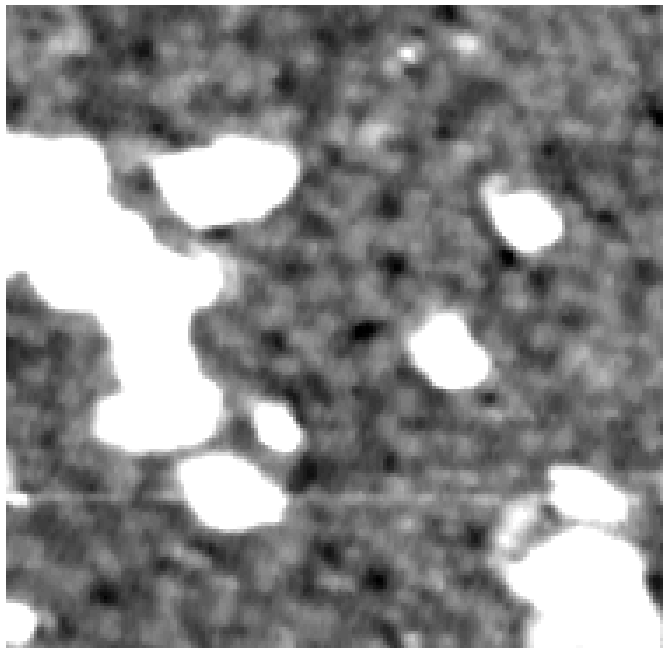
Ti/Al(111) Model System

Ti deposition on Al(111) - STM

Θ^{Ti}_{nom} = 0.05 ML



Θ^{Ti}_{nom} = 0.3 ML



Strong spectroscopic contrast, absent on Al(111). **Identification:** STM & DFT.

Randomly dispersed near-surface Ti.
Some **clustering/ordering** at higher coverage.

- H_2 dissociation on these sites?

FOV: 23 nm.
Ti/Al(111) deposited at 400 K.

2) Formation of Mobile Species - Surface Alanes

FT-IR Spectroscopy - atomic H/Al(111)

Hydride/alane related IR modes:

A - Terminal (ν_{H-T} = 1895 cm^{-1}): Ad-Al-H.

- Bridging (ν_{H-B} = 1500 cm^{-1} - 1800 cm^{-1}): higher alanes: Al_2H_6, Al_3H_9, etc.

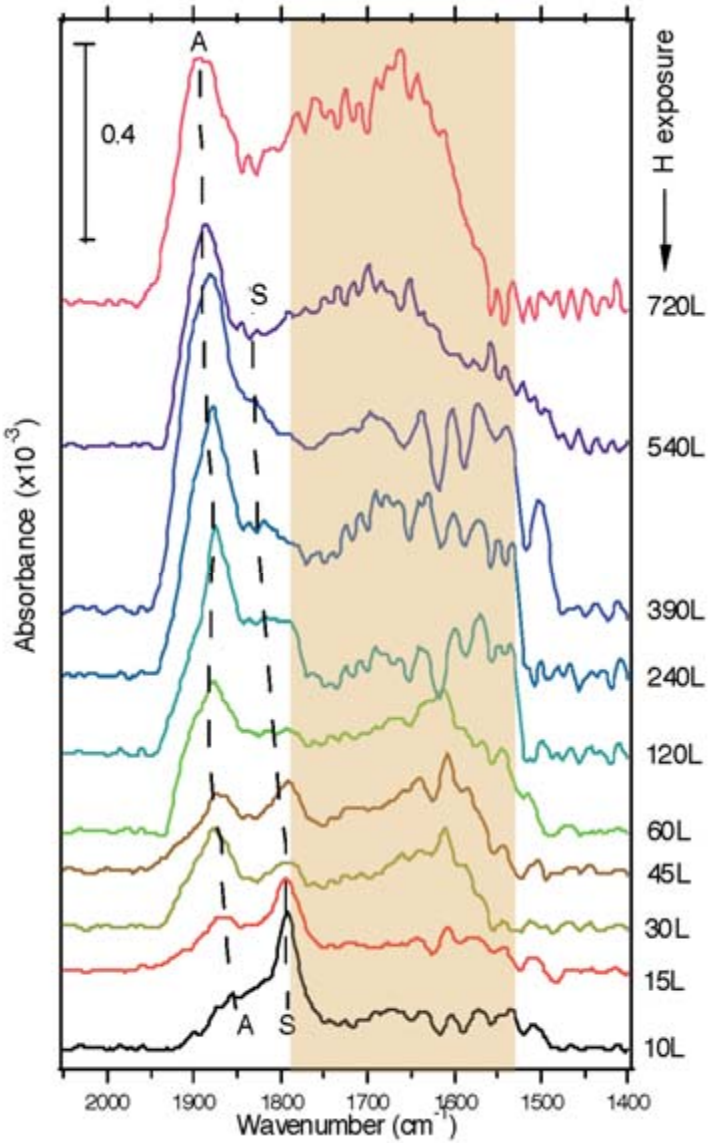
S - Additional mode at low coverage: Ad-Al-H at step edges?*

*Go et al., Surf. Sci. 437, 377 (1999).

Or: signature of small alanes?

Progressive formation of **surface alanes.**

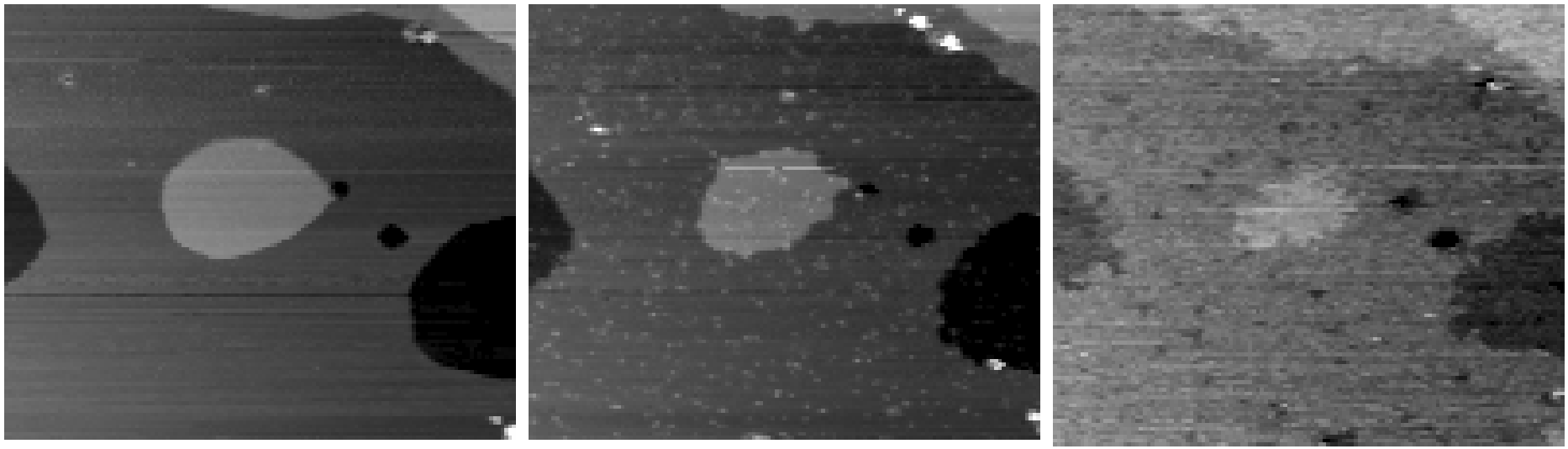
Sample: Al(111) single crystal.
Atomic-H from W-filament; T = 90 K;
H_2 dose: 10 L to 720 L; about 1% atomic-H



Atomic-H on Al(111)

STM Imaging

Al(111) | **300 L H*** | **1500 L H**



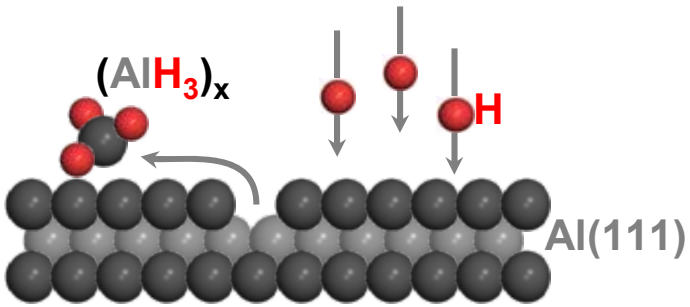
- Pronounced **etching** of surface steps.
- Evolution of population of adsorbates: **IR ⇒ surface alanes**.

*<1% atomic H
FOV: 120 nm
T = 300 K

Atomic-H on Al(111)

STM Imaging - Spectroscopic contrast

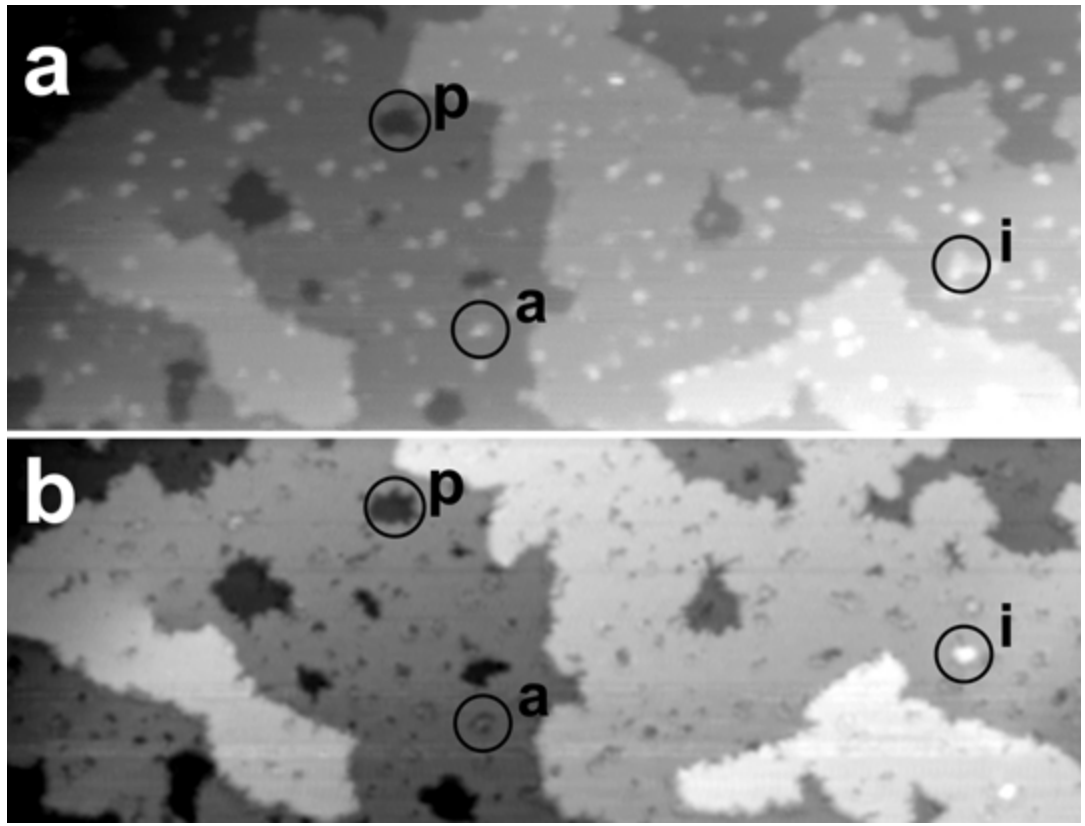
- Step etching.
- Evolution of surface alanes.



Spectroscopic identification: STM tip functionalization.

a - Clean W-tip.

b - Alane-*"functionalized"* tip.



FOV: 150 nm.
Sample: Al(111).
Atomic H: ~ 4 ML H, T = 200 K.

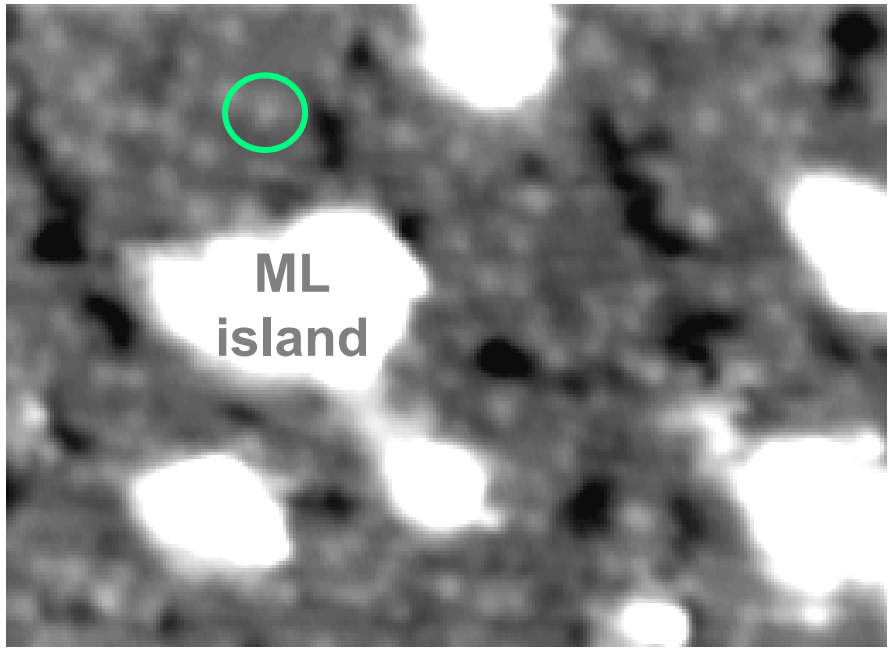
Alane Formation on Ti/Al(111)

Atomic-H on Ti/Al(111)

Θ^{Ti} = 0.05 ML
Pronounced alane evolution.

Θ^{Ti} = 0.25 ML
No step etching.
No evolution of surface alanes.

But: New electronic signatures
○ 0.05 Å 'protrusions'.



High Ti coverages: near-surface Ti strongly binds Al.

⇒ **Saturation effects** at high Ti concentrations.
⇒ **Incomplete re-hydrogenation:** residual Ti-rich Al grains?

FOV: 20 nm
0.25 ML Ti/Al(111)
~ 4 ML H, T = 200 K.

Future Plans

Near Term Objectives:

1) Identify stable near-surface Ti:Al structures & active complexes for H_2 dissociation (Spectroscopic STM, DFT).
2) Quantify H_2 dissociation by Ti:Al (STM, IR, DFT).

Future Research - all based on strong interaction experiment-theory

3) Establish kinetics of alane formation (T-dependent STM, IR).
3) Compare & quantify Al and $(AlH_3)_x$ mass transport (real-time LEEM).
4) NaH/Al: Kinetics of re-hydrogenation to Na_3AlH_6 (LEEM).
5) Test concepts using bulk synthesis and characterization.

Fundamental understanding of Ti-catalyzed reversible hydrogen storage in sodium alanate.

***Design rules* for new reversible hydride materials.**

BNL - Center for Functional Nanomaterials

www.cfn.bnl.gov

One of five new DOE Nanoscale Science Research Centers,
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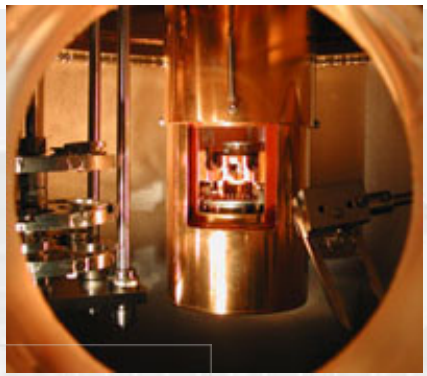
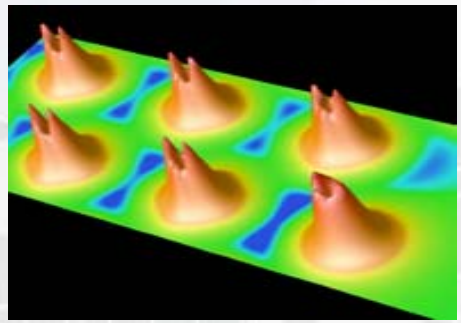
Nano-Patterning
John Warren
Chris Jacobsen, SBU



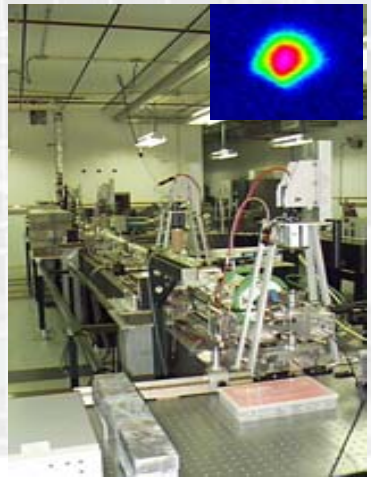
Proximal Probes
Peter Sutter

Theory & Computation
Jim Davenport



Electron Microscopy
Yimei Zhu

NSLS *Ron Pindak*

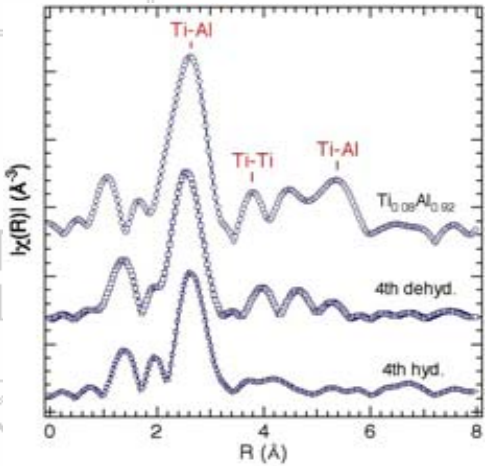


Ultra-fast Optical Sources
Alex Harris

BNL - National Synchrotron Light Source

X-ray & VUV beamlines - Examples:

- **X-ray absorption spectroscopy:**
  EXAFS, NEXAFS.
- **X-ray diffraction:**
  Powder, time-resolved, high-pressure.
- **X-ray microprobe**
- **IR micro-spectroscopy**
- **Surface microscopy & spectroscopy**
  Photoemission microscopy (PEEM).



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