Studies of Size Selected Model Catalysts:

Hydrazine decomposition over size selected Ir_n/Al_2O_3 model catalysts

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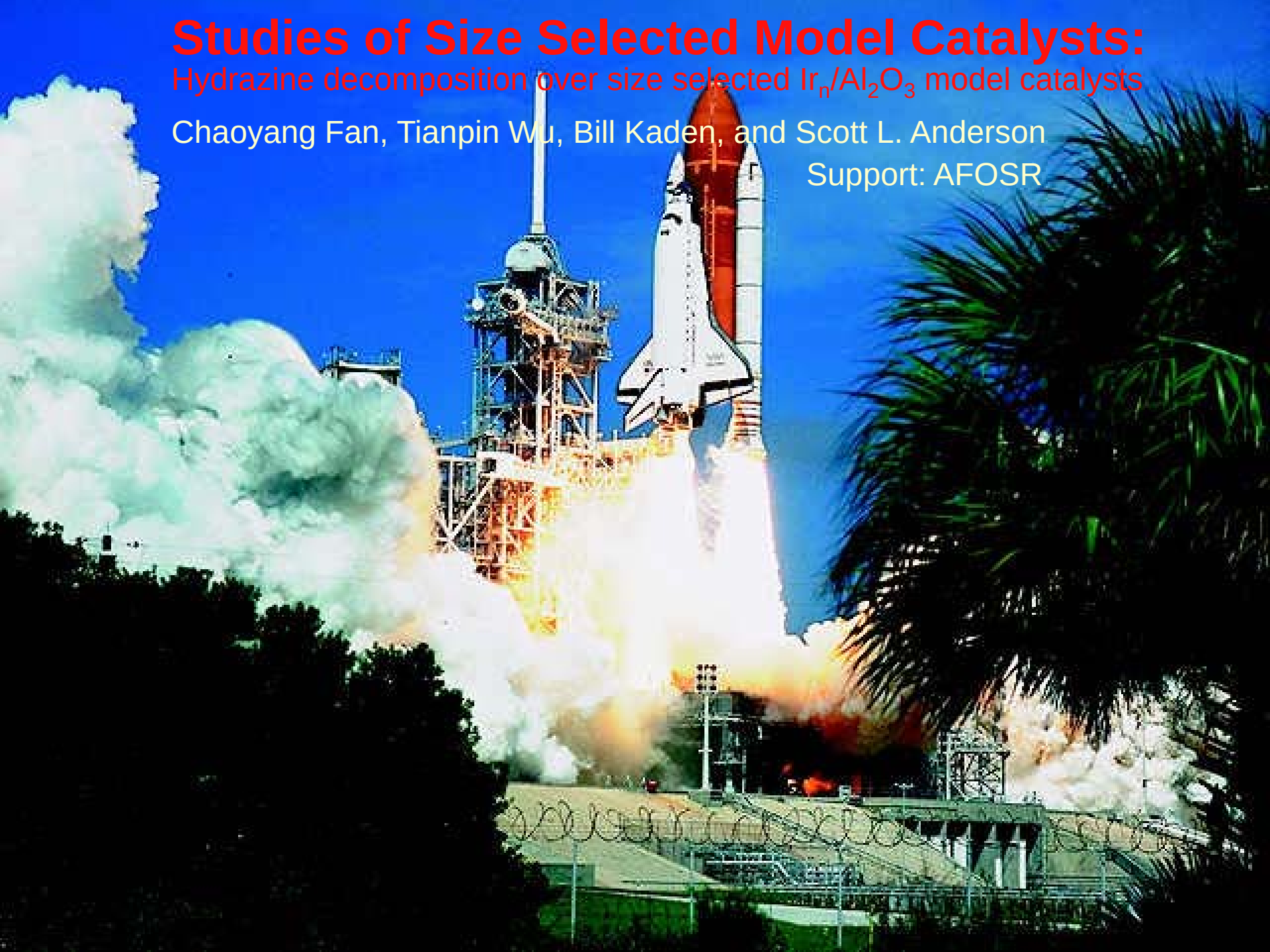
Support: AFOSR



Background

- Overview of Experiment:
  - What do we do?
    - Attempt to further understand the chemistry taking place on catalytic surfaces.
    - We try to develop an understanding of the dependence of catalysis on cluster size.
  - How do we do it?
    - Beamline: Catalytic surfaces of interest are created by depositing various size selected metal nano-clusters onto various substrate materials.
    - UHV Chamber (Base Pressure ~ $3x10^{-10}$ torr): Prepared surfaces are analyzed and tested using an assortment of surface sensitive techniques.

Hydrazine/Ir/alumina

Why Hydrazine?

- Spacecraft thrusters, gas generators, power generation
- H_2 storage (CO free for fuel cells)

Problems:

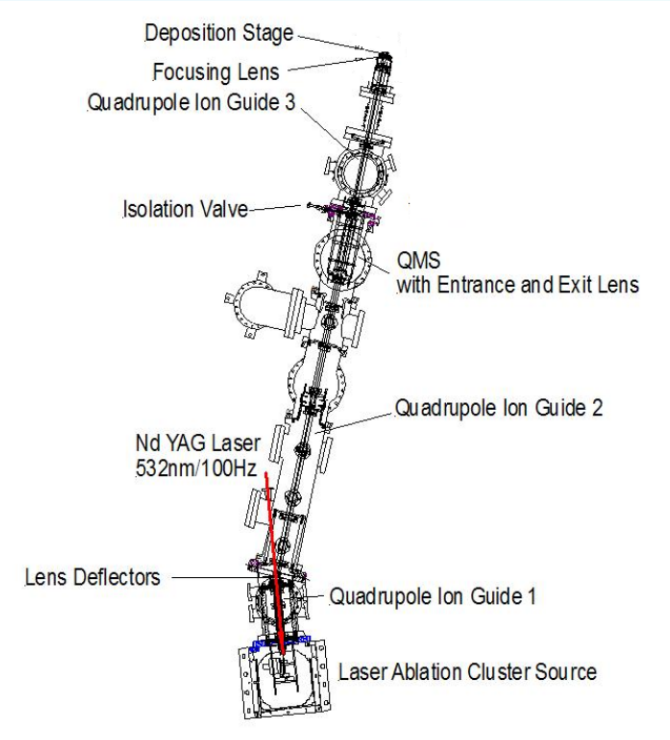
- Sintering, support degradation
  - High T stability (high T_{melt})
- Cold starts
  - Low T chemistry (low E_a)

	E_a (kJ)	m.p.(K)
Pd	67	1827
Pt	71	2045
Rh	50	2239
Ir	50	2680
Nb		2741
Re	~57	3453
W	~60	3680
SiO_2		>1800
Al_2O_3		2288
MgO		3125

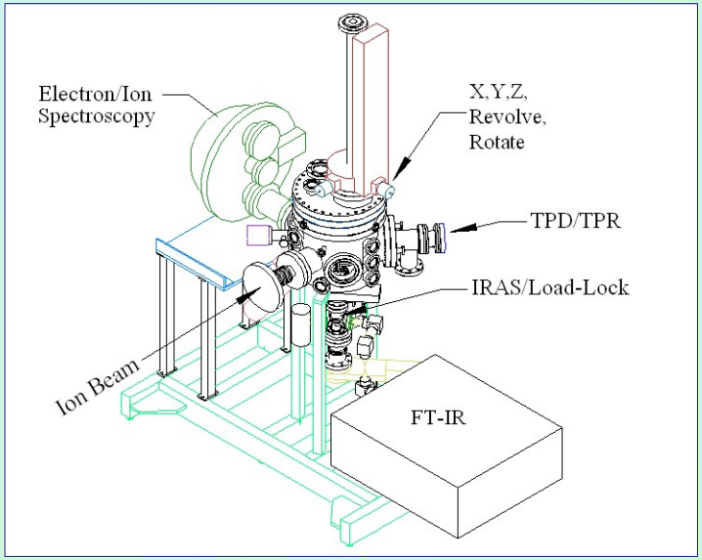
Characterize low temperature chemistry v.s. Ir_n size
Characterize sintering behavior
Develop strategies for improvements

Instrument Design

Beamline



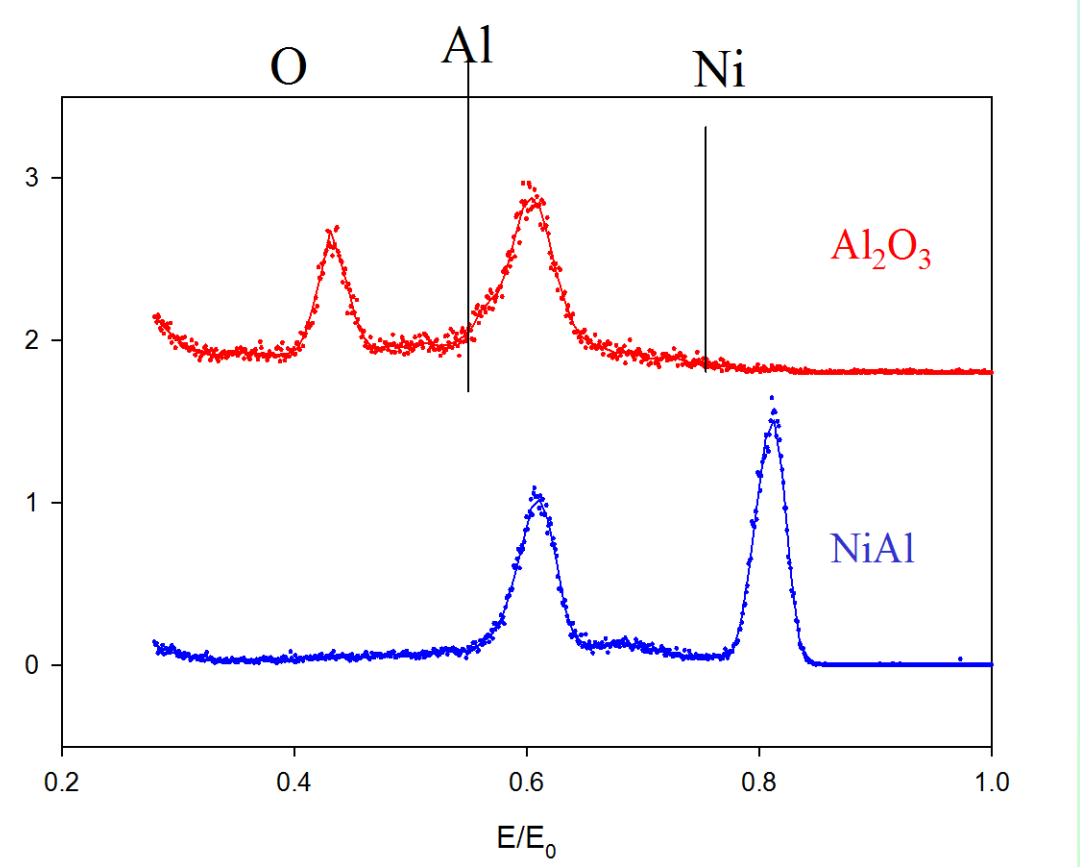
UHV Chamber



Once prepared, we can probe the model catalyst with our surface sensitive techniques.

Metal clusters form within the source box in the presence of Helium after being vaporized by incoming laser radiation. Cation clusters are selectively guided through the beamline by a series of quadrapole ion guides and lenses. Cluster sizes of interest are selectively allowed to pass through the mass selector and be deposited on the substrate of interest within the UHV chamber.

Preparation of Al_2O_3/NiAl(110)



Freund recipe:

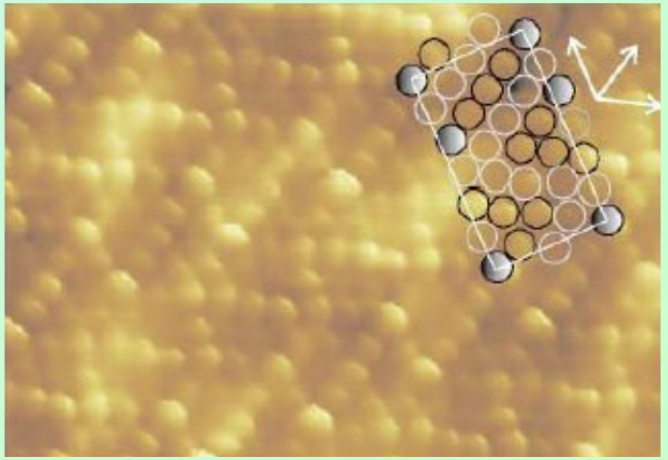
1.Ar^+ Sputter NiAl (110)

2.Anneal: 1000K, 20 min

1220K, 10 min

3.O_2 120L at 550K

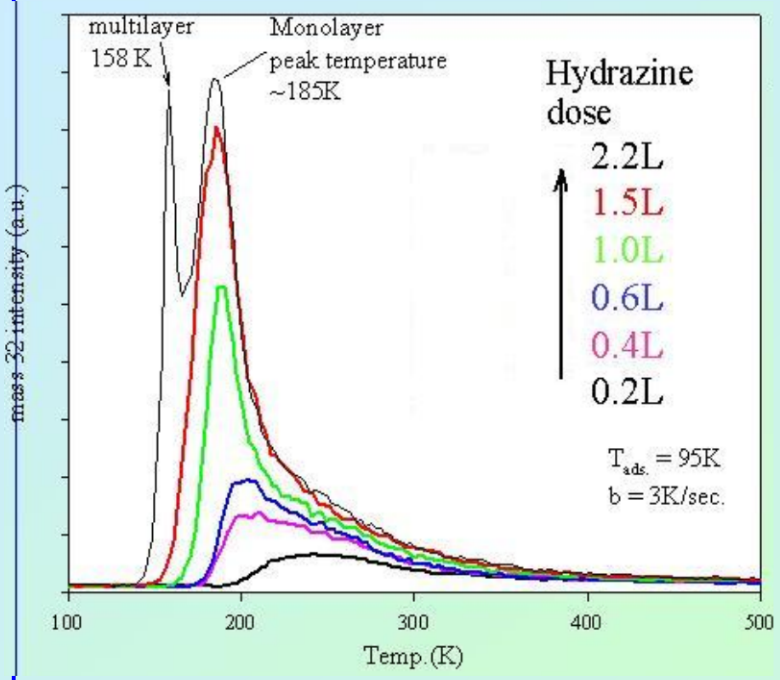
4.Anneal: 950K, 10 min

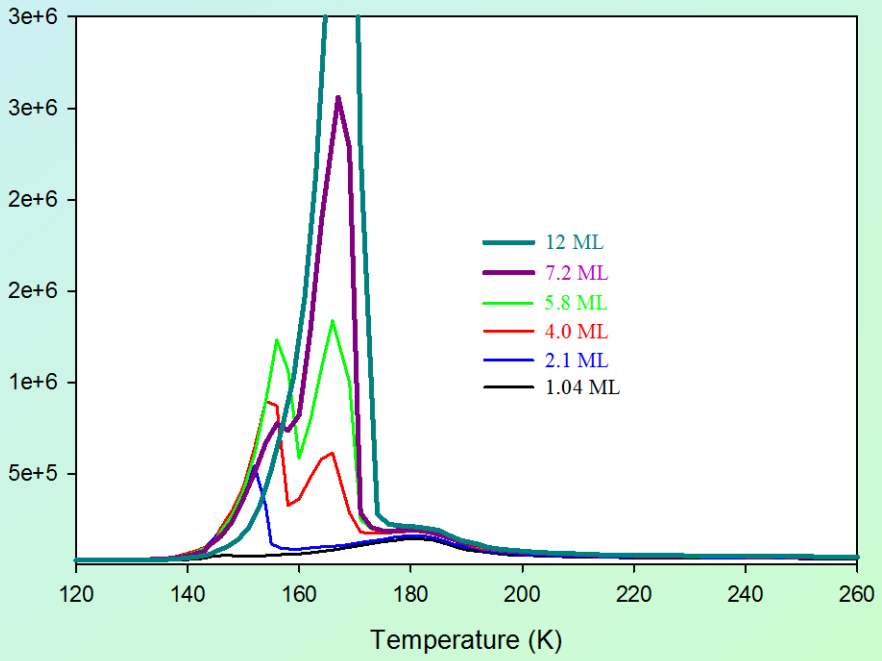


O-terminated, 5 Å thick

Kulawik et al., PRL (2003) 256101

Hydrazine/Alumina/NiAl(110)





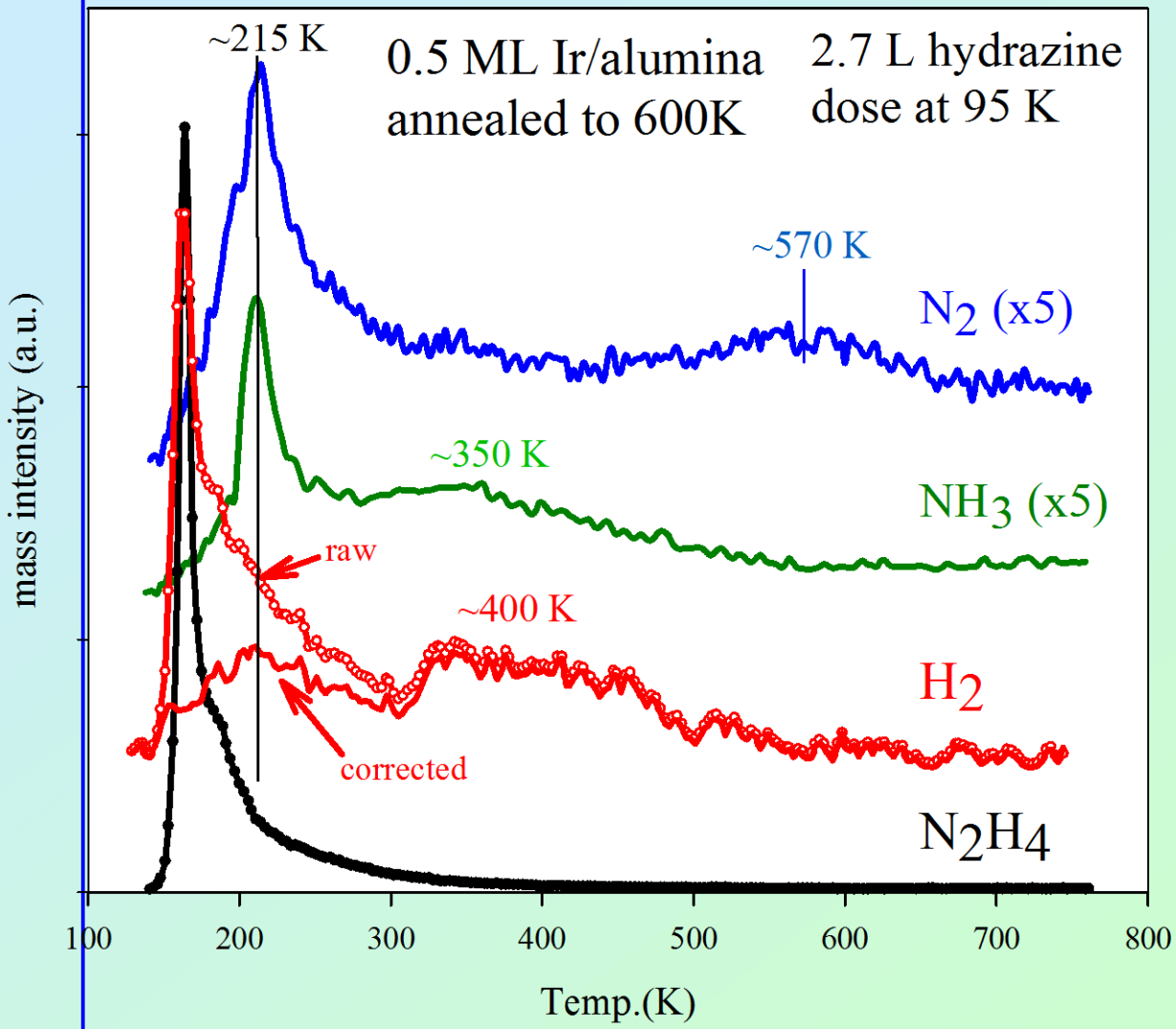
No previous data on N_2H_4/Ir/alumina below room temperature.

The multilayer desorbs intact providing us with an internal standard for the hydrazine cracking pattern.

With increasing coverage, a third peak forms with more binding energy than the original multilayer. This could signal the onset of a phase transition within the hydrazine multilayer.

Hydrazine TPD from High Coverage Model Catalyst

High coverage catalyst similar to bulk metal



0.5 ML Ir/alumina, annealed to make clusters

Low T

$N_2H_{4\ ads} \rightarrow \mathbf{N_2}\uparrow + 4H_{ads}$

$2H_{ads} + N_2H_{4\ ads} \rightarrow \mathbf{2NH_3}\uparrow$

$2H_{ads} \rightarrow \mathbf{H_2}\uparrow$

$N_2H_{4\ ads} \rightarrow 2\mathbf{NH_2}$

Higher T

$NH_{2\ ads} \rightarrow NH_{ads} + H_{ads}$

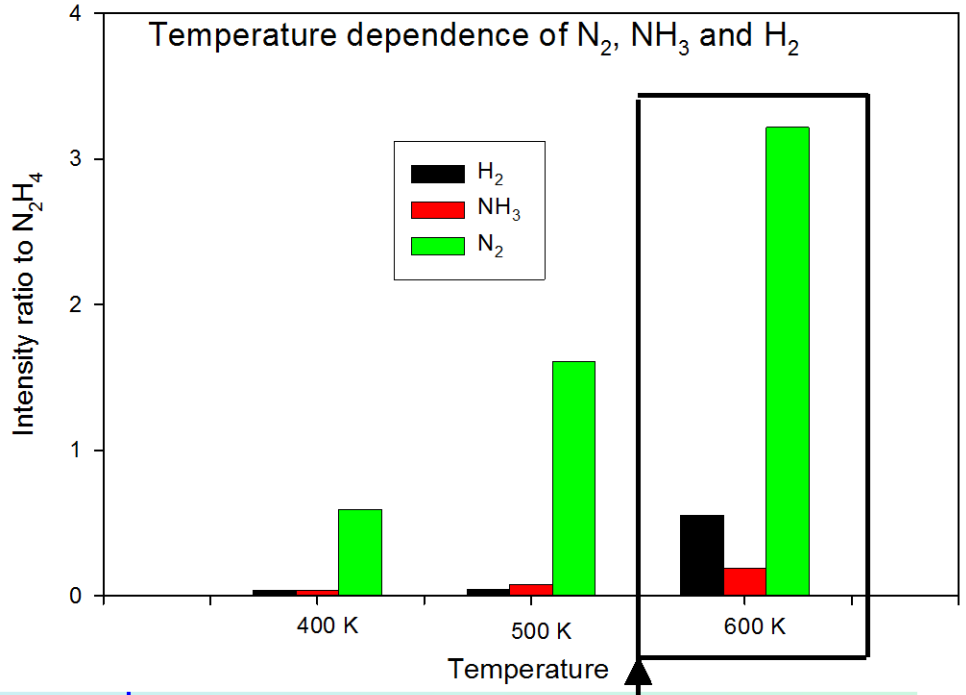
$NH_{ads} \rightarrow N_{ads} + H_{ads}$

$H_{ads} + NH_{2\ ads} \rightarrow \mathbf{NH_3}\uparrow$

$2H_{ads} \rightarrow \mathbf{H_2}\uparrow$

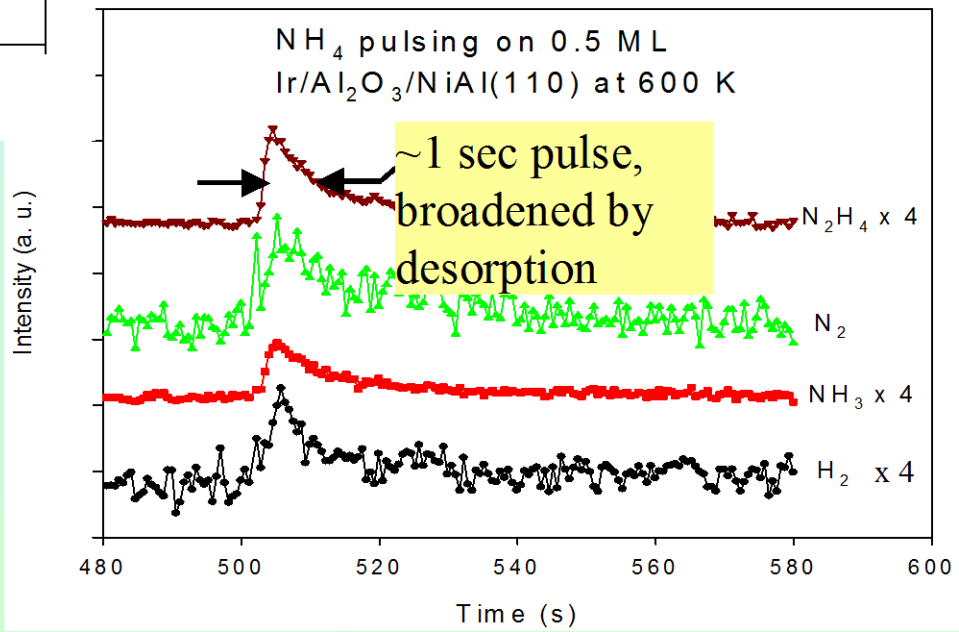
$2N_{ads} \rightarrow \mathbf{N_2}\uparrow$

Hydrazine Pulse Dosing

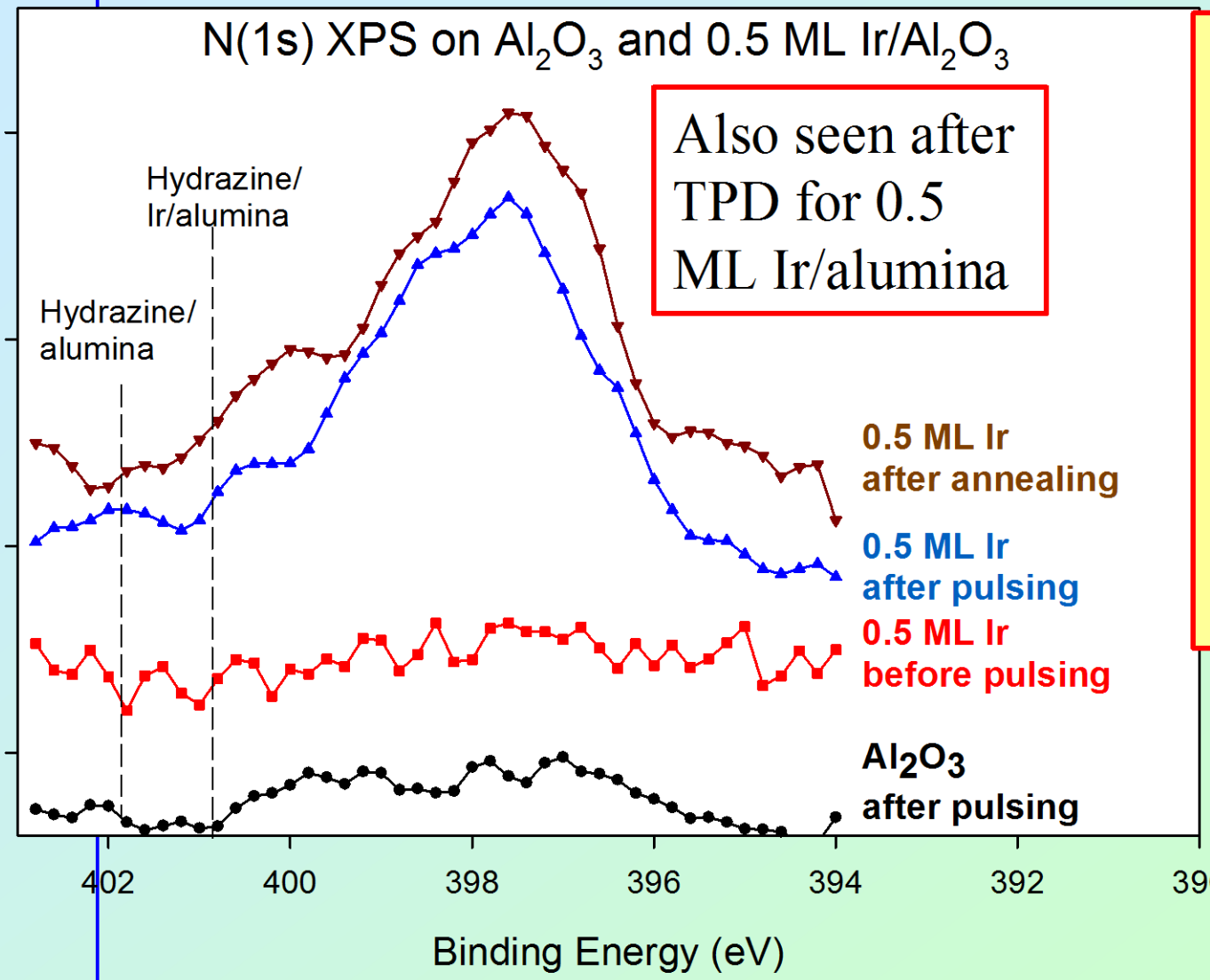


Hydrazine pulsed onto catalyst while potential products leaving the surface are monitored with a mass spectrometer.

Same Data Set



N 1s XPS

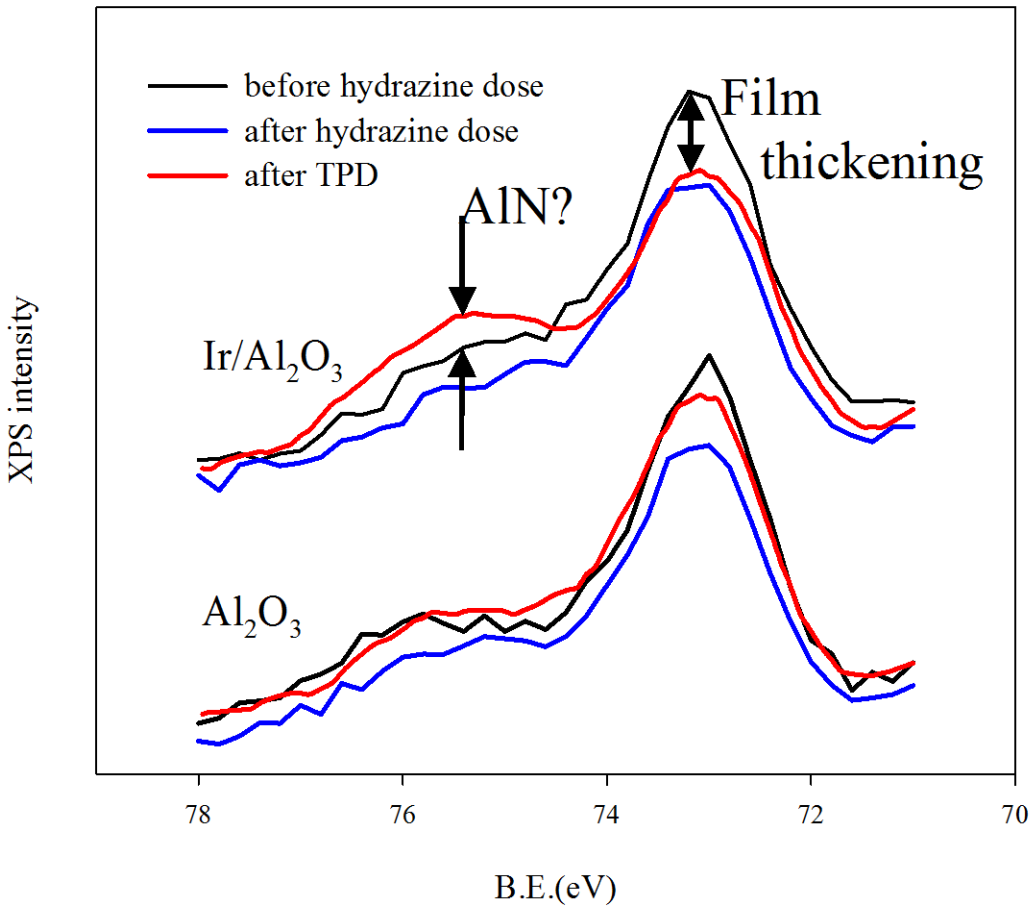


398 eV B.E.
cyanide or nitride

No C signal
∴ Nitride

No change in Ni or Ir XPS

Nitride Formation

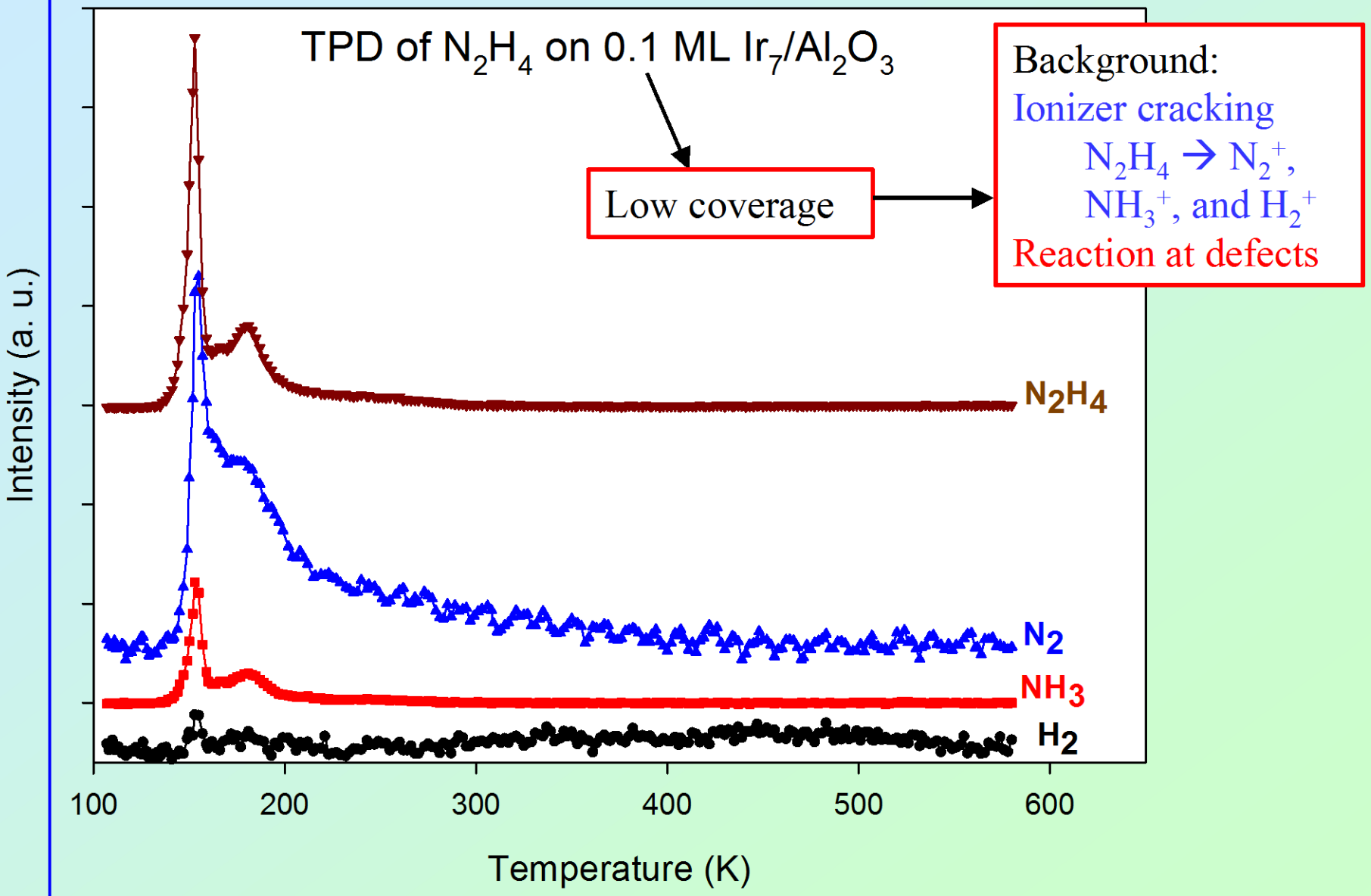


$Al_xO_yN_z$ compound

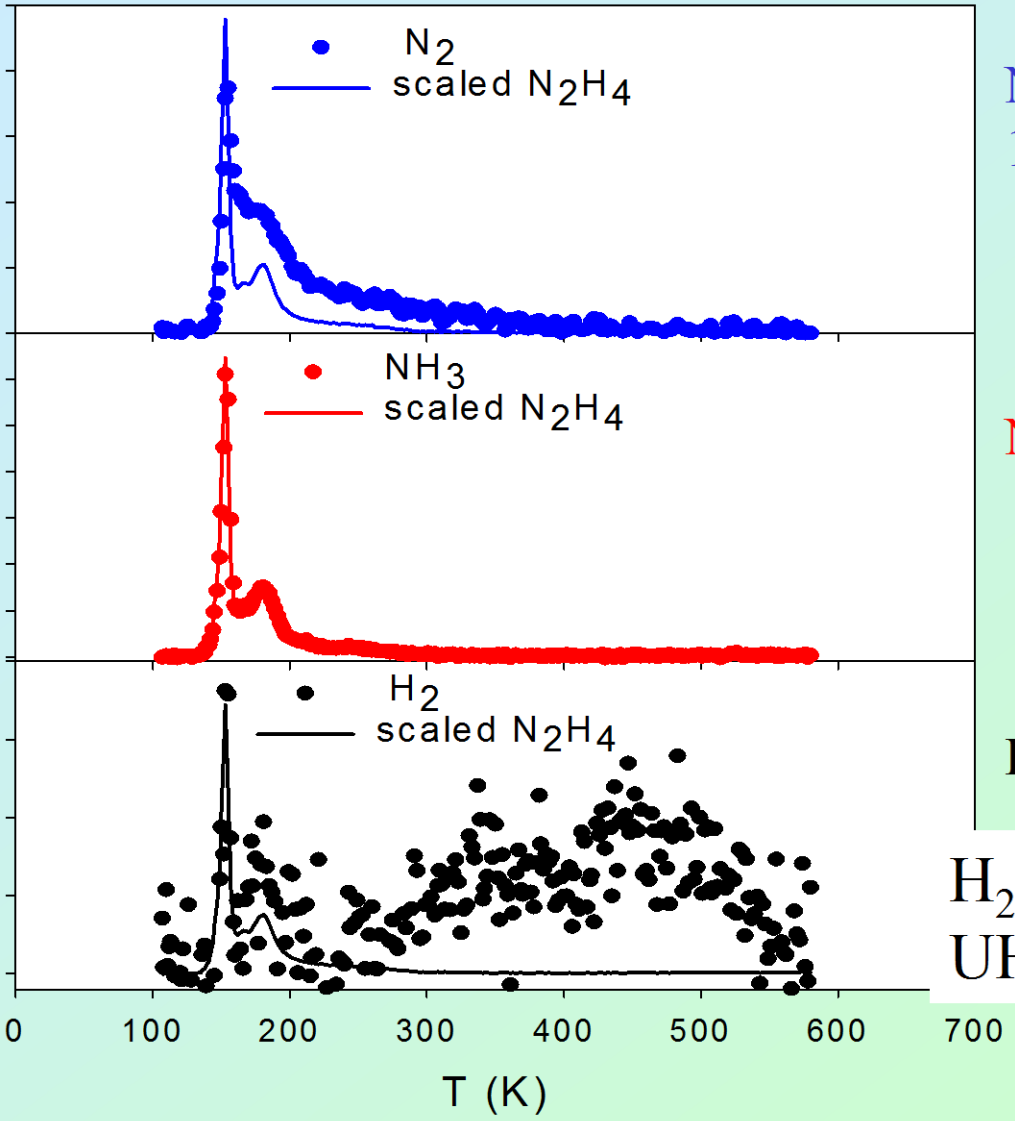
No change in O 1s signal
No change in O ISS

No N ISS signal after TPD
-Sub-surface nitride

Raw TPD $N_2H_4/Ir_7/alumina$



Correcting for N_2H_4 cracking



N_2 production in range from 155 K to ~350 K

215 K for high coverage

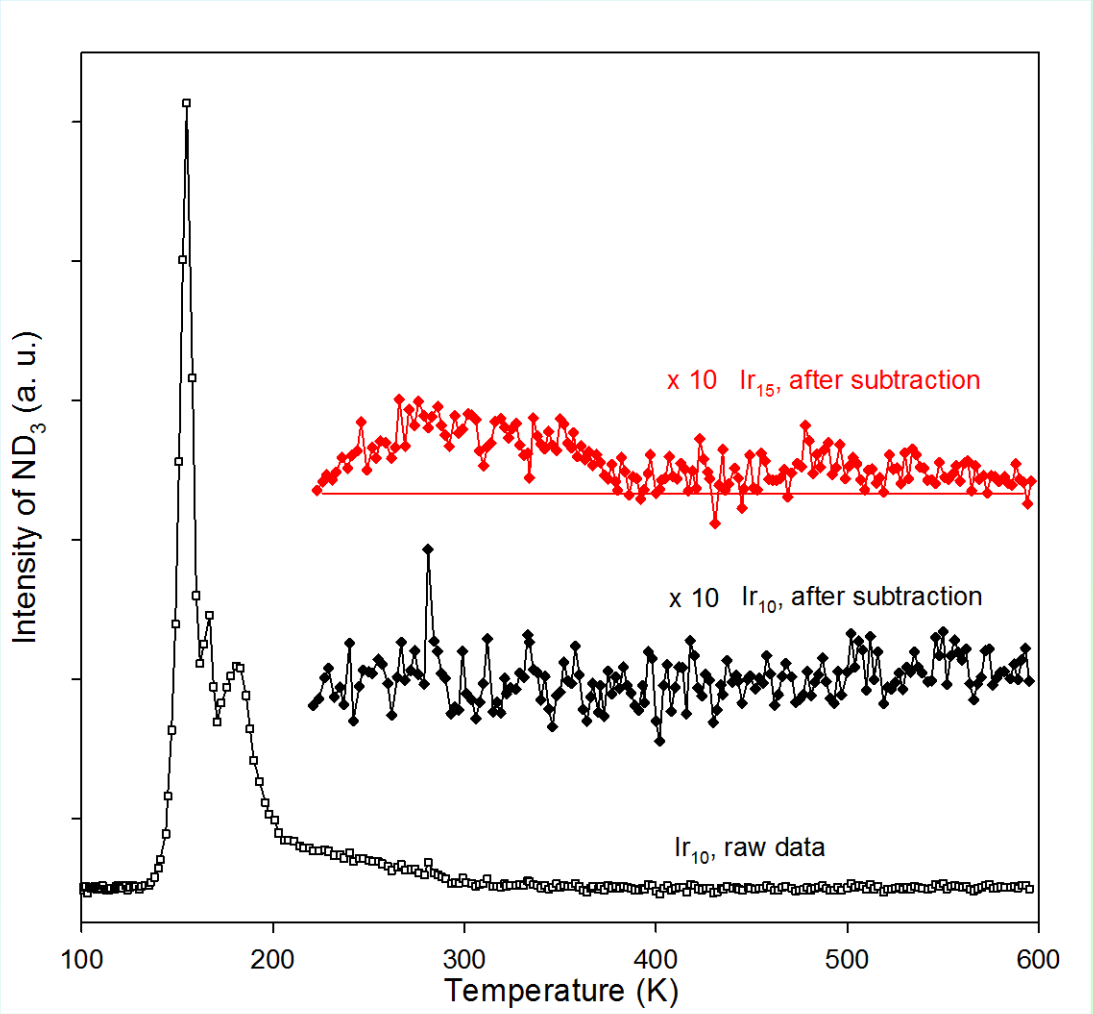
No NH_3 from Ir_7/alumina

NH_3 similar to N_2 for high coverage

H_2 production ~275 – 550 K

H_2 background high in UHV – switch to N_2D_4

ND_3 Production from $Ir_n/Al_2O_3/NiAl$



High coverage v.s. Small Clusters

0.5 ML Ir/alumina, annealed to make clusters

Low T

$N_2H_{4\ ads} \rightarrow N_2\uparrow + 4H_{ads}$

$2H_{ads} + N_2H_{4\ ads} \rightarrow 2NH_3\uparrow$

$2H_{ads} \rightarrow H_2\uparrow$

$N_2H_{4\ ads} \rightarrow 2NH_2$

Higher T

$NH_{2\ ads} \rightarrow NH_{ads} + H_{ads}$

$NH_{ads} \rightarrow N_{ads} + H_{ads}$

$H_{ads} + NH_{2\ ads} \rightarrow NH_3\uparrow$

$2H_{ads} \rightarrow H_2\uparrow$

$2N_{ads} \rightarrow N_2\uparrow$

$N_{ads} \rightarrow$ **Nitride Formation**

Size Selected Ir_n/alumina

Low T

$\mathbf{N_2H_{4\ ads} \rightarrow N_2\uparrow + 4H_{ads}}$

$2H_{ads} + N_2H_{4\ ads} \rightarrow 2NH_3\uparrow$

$2H_{ads} \rightarrow H_2\uparrow$

$N_2H_{4\ ads} \rightarrow 2NH_2$

Higher T

$NH_{2\ ads} \rightarrow NH_{ads} + H_{ads}$

$NH_{ads} \rightarrow N_{ads} + H_{ads}$

$H_{ads} + NH_{2\ ads} \rightarrow NH_3\uparrow (Ir_{15})$

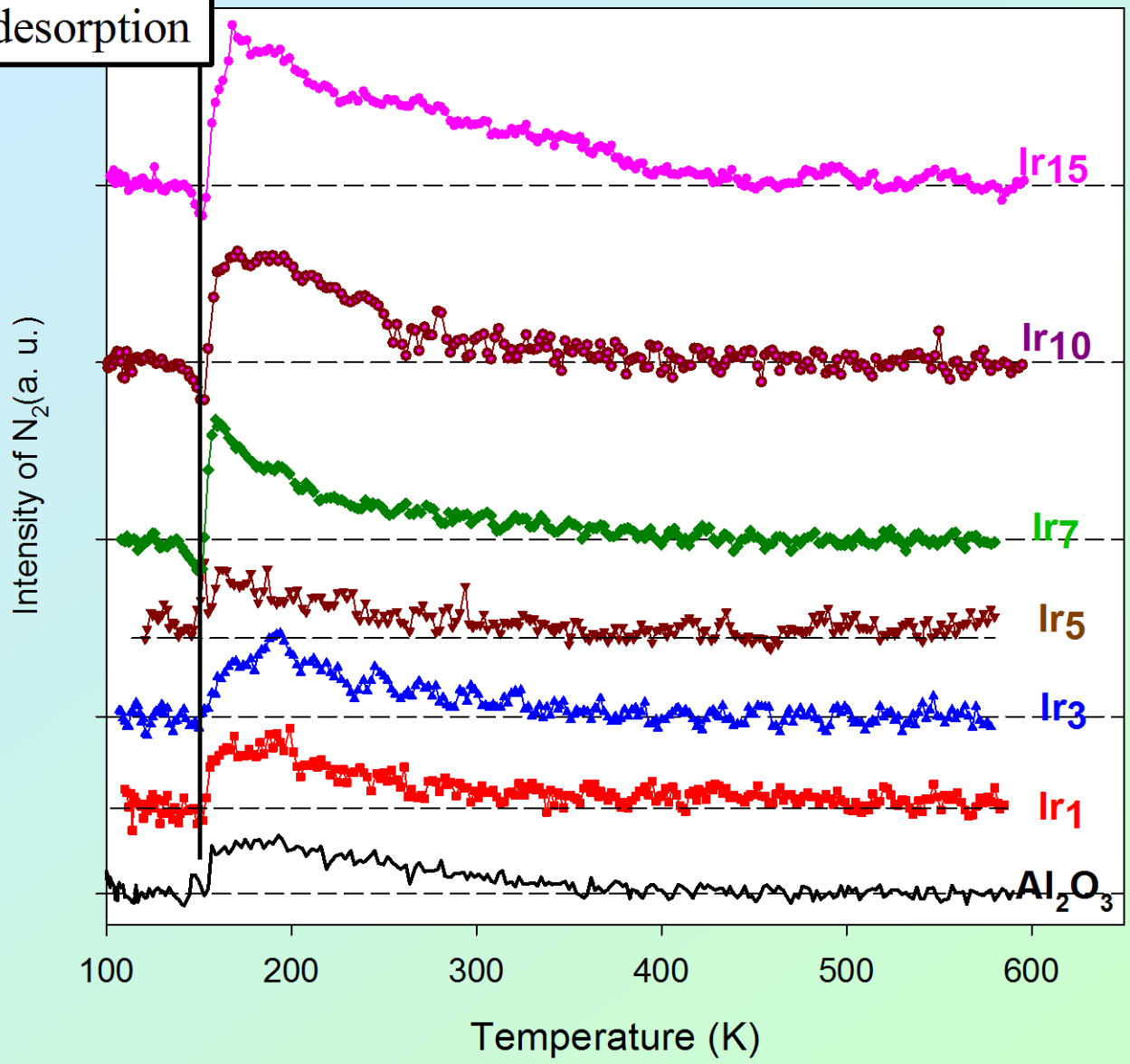
$\mathbf{2H_{ads} \rightarrow H_2\uparrow}$

$2N_{ads} \rightarrow N_2\uparrow$

Little Nitride formation

N_2 TPD from Ir_n/alumina

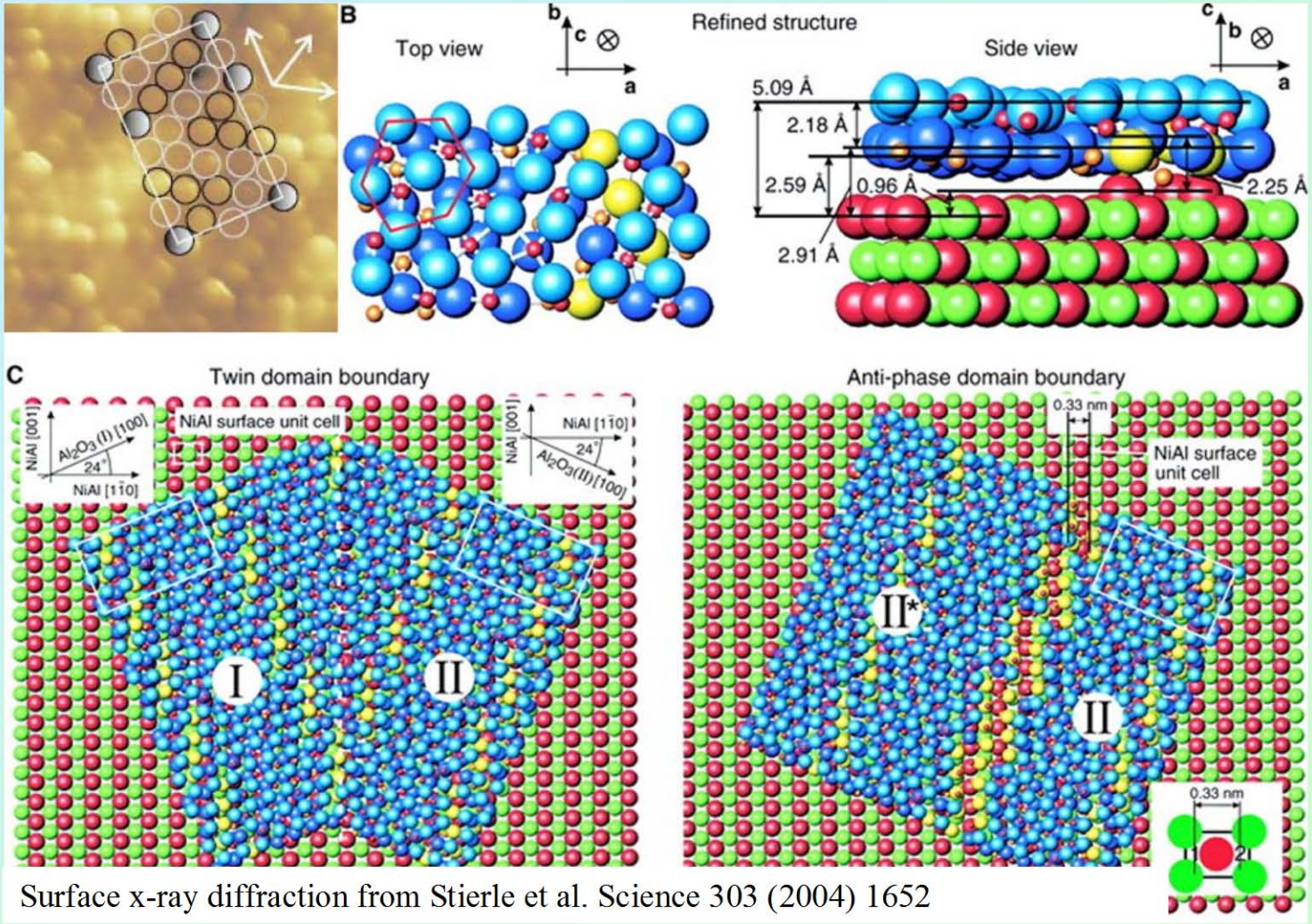
Sub-surface layer desorption



Hydrazine cracking contribution subtracted

alumina/NiAl(110) structure

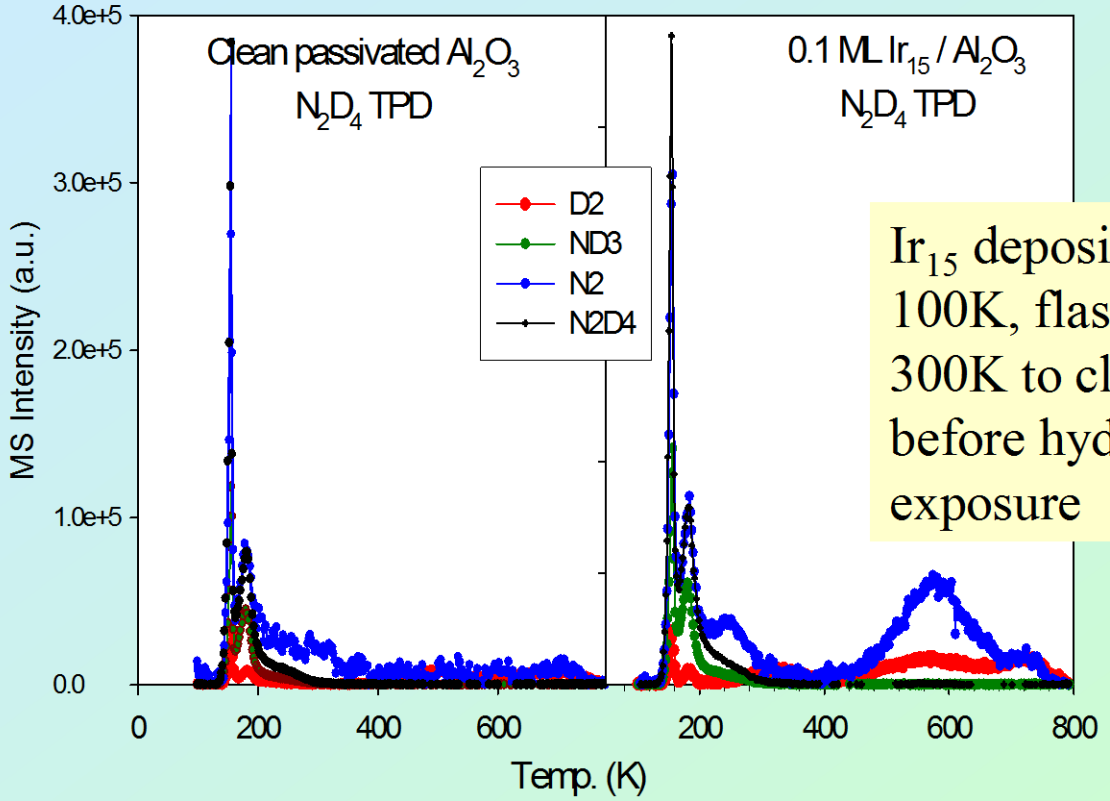
STM from Kulawik et al. PRL (2003) 256101



Surface x-ray diffraction from Stierle et al. Science 303 (2004) 1652

Gaps between Al_2O_3 film and NiAl substrate give rise to sub surface nitrides when dosing w/ N_2H_4

Passivated Alumina/NiAl(110)

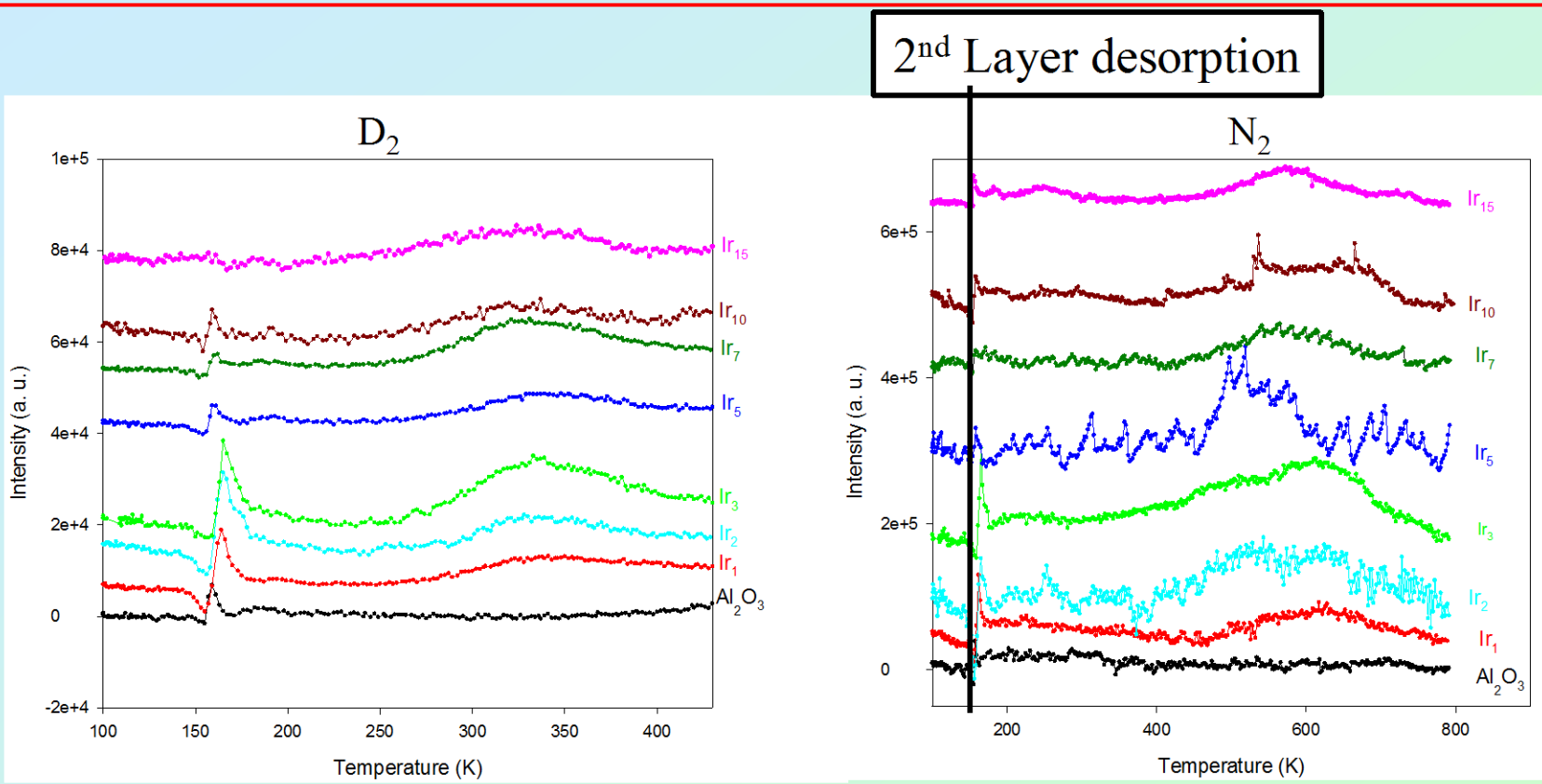


Ir_{15} deposited at 100K, flashed to 300K to clean before hydrazine exposure

Small N 1s signal 398 eV:
No N ISS or other changes
Sub-surface Nitride
Much less efficient w/o Ir
Repeated cycles

Repeat until TPD reaches steady state
Dose ~10 ML N_2D_4 at ~100K
TPD to 800 K (desorbs everything)
Deposit clusters
TPD of Ir_n/passivated Alumina

D_2 and N_2 Production from Ir_n/Alumina (passivated)



High temperature peaks are present for N_2 in the passivated catalyst

Peak intensity and temperature is size-dependent for both products

High coverage v.s. Small Clusters

0.5 ML Ir/alumina, annealed to make clusters

Low T

$N_2H_{4\ ads} \rightarrow N_2\uparrow + 4H_{ads}$

$2H_{ads} + N_2H_{4\ ads} \rightarrow 2NH_3\uparrow$

$2H_{ads} \rightarrow H_2\uparrow$

$N_2H_{4\ ads} \rightarrow 2NH_2$

Higher T

$NH_{2\ ads} \rightarrow NH_{ads} + H_{ads}$

$NH_{ads} \rightarrow N_{ads} + H_{ads}$

$H_{ads} + NH_{2\ ads} \rightarrow NH_3\uparrow$

$2H_{ads} \rightarrow H_2\uparrow$

$2N_{ads} \rightarrow N_2\uparrow$

$N_{ads} \rightarrow$ **Nitride Formation**

Size Selected Ir_n/alumina PASSIVATED

Low T

$\mathbf{N_2H_{4\ ads} \rightarrow N_2\uparrow + 4H_{ads}}$

$2H_{ads} + N_2H_{4\ ads} \rightarrow 2NH_3\uparrow$

$2H_{ads} \rightarrow H_2\uparrow$

$N_2H_{4\ ads} \rightarrow 2NH_2$

Higher T

$NH_{2\ ads} \rightarrow NH_{ads} + H_{ads}$

$NH_{ads} \rightarrow N_{ads} + H_{ads}$

$H_{ads} + NH_{2\ ads} \rightarrow NH_3\uparrow$

$\mathbf{2H_{ads} \rightarrow H_2\uparrow}$

$2N_{ads} \rightarrow N_2\uparrow$

Nitride already formed

What's Next

Hydrazine/Ir/Alumina

- Fine tune the passivation process
- Finish Ir_n TPD - When does NH_3 production kick in (new quad)
- Pulse dosing with Ir_n
- NH_3 and H_2 TPD / decomposition for comparison
- IRAS of N_2H_4 and NH_x v.s. cluster size
- ISS and XPS of as-deposited, reacted, and sintered clusters.