제 24회 한국반도체학술대회
세션: [TC1-G] Device Physics and Characterization 1

DFT study on the clean-up mechanism of InGaAs(001) native oxides in atomic layer deposition

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Computational Materials Design

Contents

- **Introduction**
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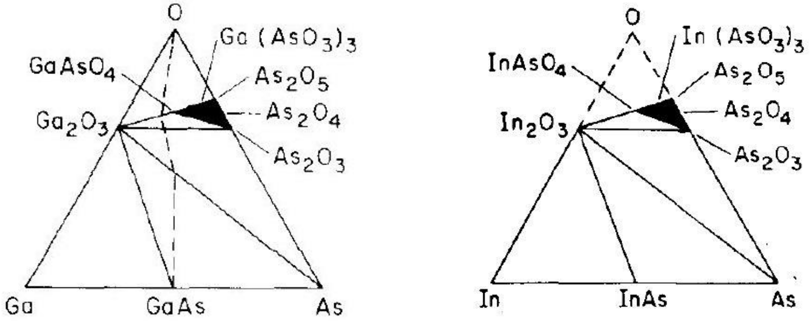
  - ALD & Self-cleaning

- **Clean-up reaction of native oxides of InAs**
  - Removal of As_2O_3 by pretreatment: thermodynamics
  - Removal of In_2O_3 by ALD: thermodynamics
  - Removal of In_2O_3 by ALD: atomic mechanism

- **Summary**

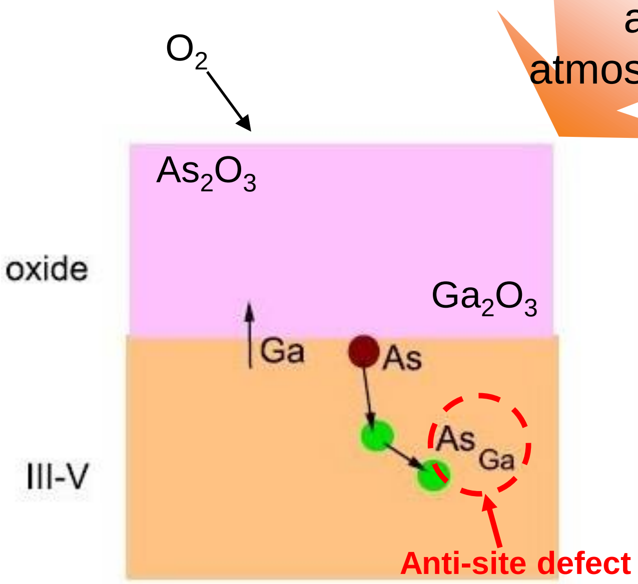
Native oxides of GaAs & InAs

Ga-As-O & In-As-O ternary phase diagram



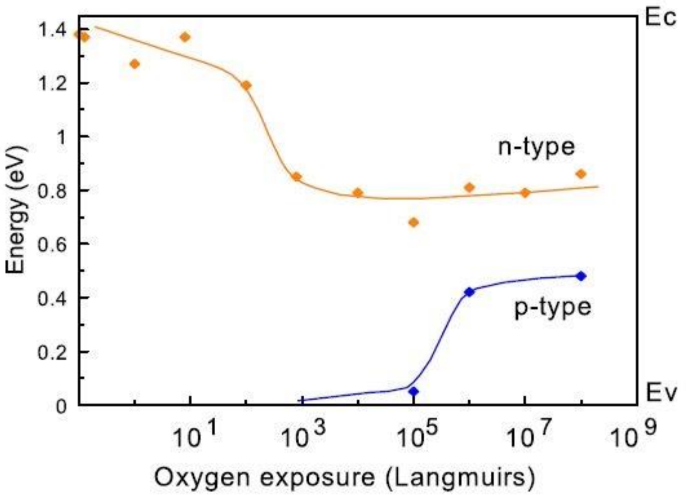
Thin Solid Film, 103, 3 (1983).

Oxidation
at
atmosphere



Generation
of
point defects

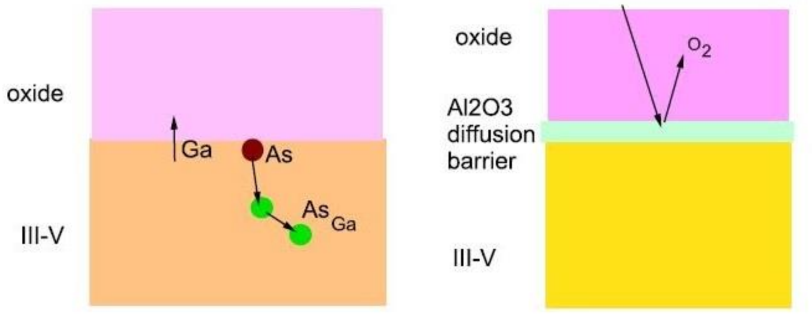
Fermi-level pinning



Phys. Rev. Lett. 44, 420 (1980).

Lower D_{it} after high-k ALD

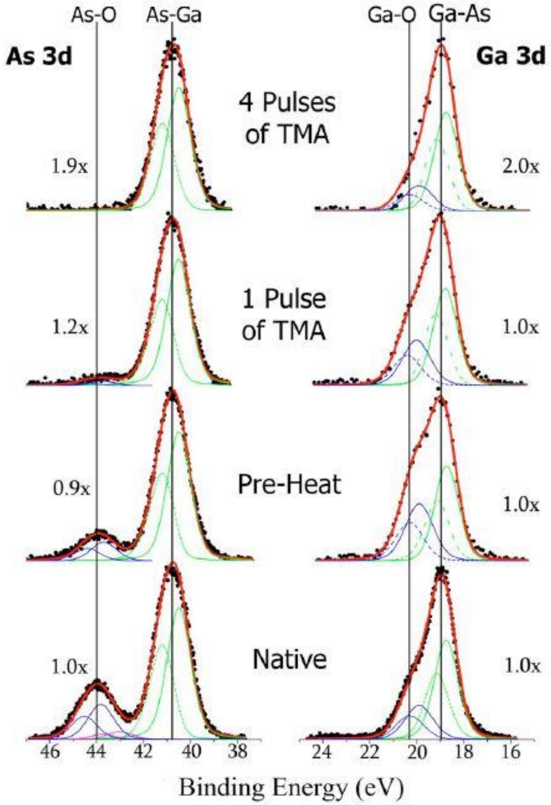
High-k oxides as diffusion barrier



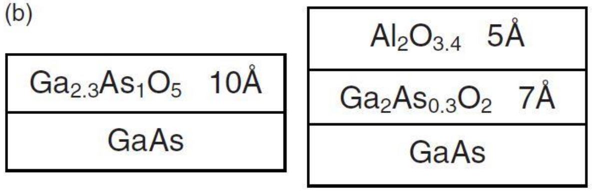
Materials Science and Engineering R 88, 1 (2015).

ALD half cycle by $Al(CH_3)_3$

Removal of native oxides



(b)

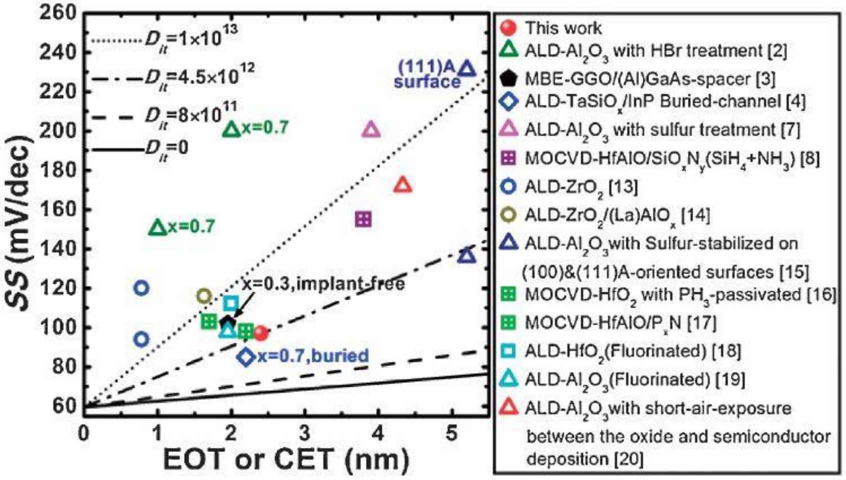


320 ° C preheated 1 TMA pulse exposed

Appl. Phys. Lett. 94, 222108 (2009).

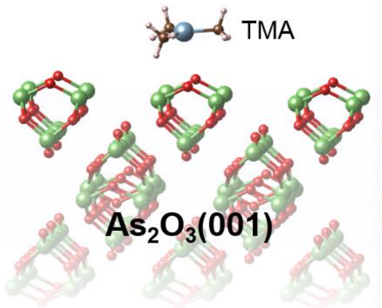
"Self-cleaning"

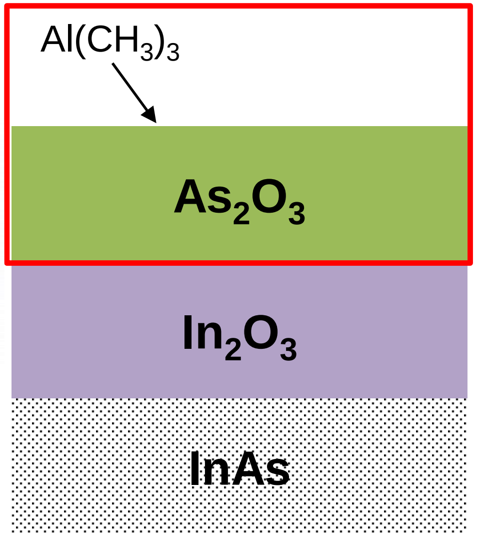
Lower D_{it} & better performance

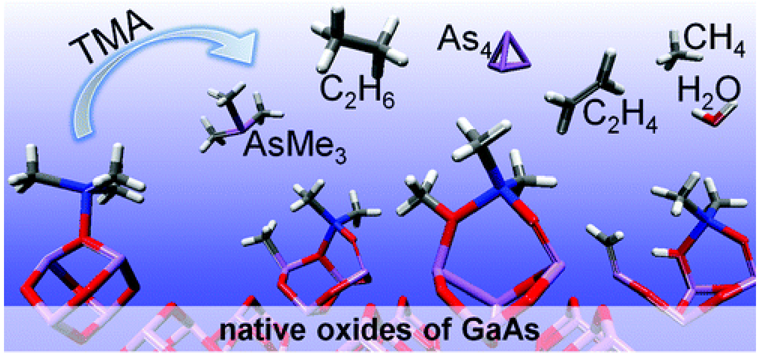


Device characterization

Modeling of the “self-cleaning”: previous study

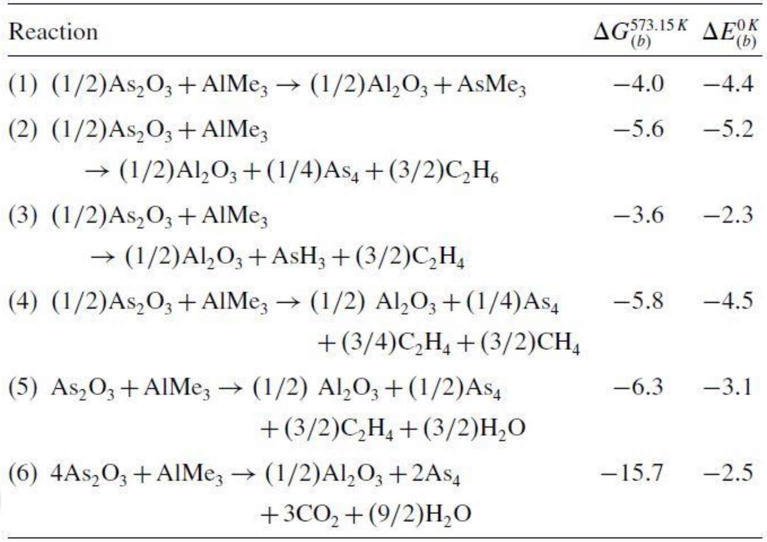




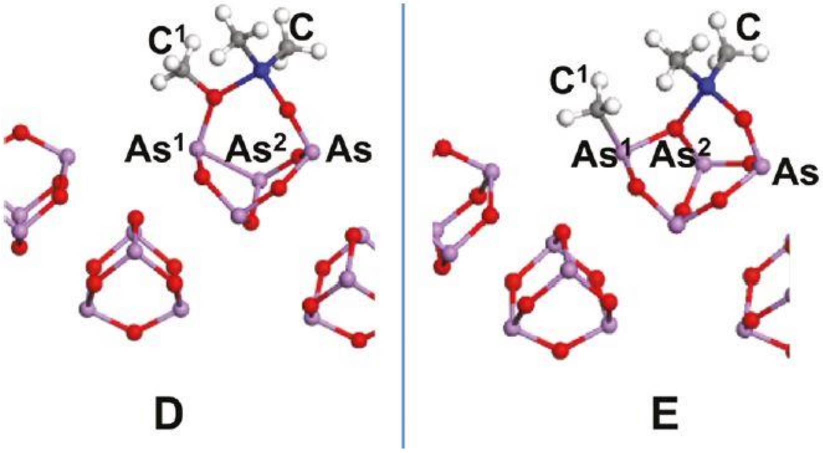


J. Nanosci. Nanotechnol. 11, 8246 (2011).
J. Phys. Chem. C 116, 643 (2012).

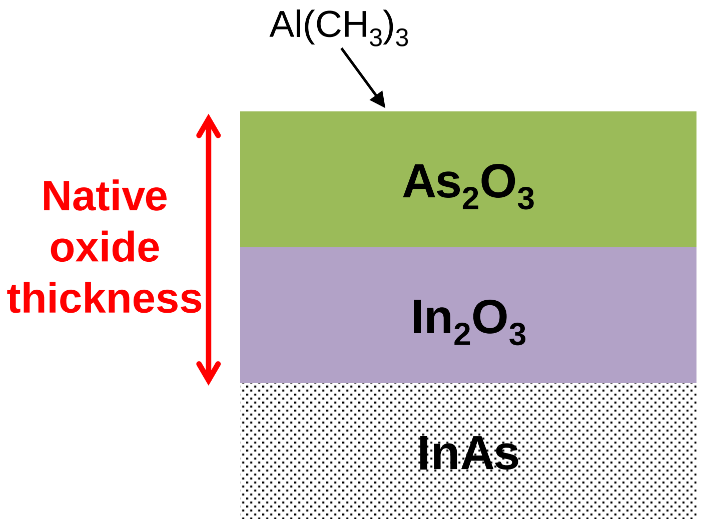
First-principles calculation



Reaction	$\Delta G^{573.15K}_{(b)}$	$\Delta E^{0K}_{(b)}$
(1) $(1/2)As_2O_3 + AlMe_3 \rightarrow (1/2)Al_2O_3 + AsMe_3$	−4.0	−4.4
(2) $(1/2)As_2O_3 + AlMe_3 \rightarrow (1/2)Al_2O_3 + (1/4)As_4 + (3/2)C_2H_6$	−5.6	−5.2
(3) $(1/2)As_2O_3 + AlMe_3 \rightarrow (1/2)Al_2O_3 + AsH_3 + (3/2)C_2H_4$	−3.6	−2.3
(4) $(1/2)As_2O_3 + AlMe_3 \rightarrow (1/2)\ Al_2O_3 + (1/4)As_4 + (3/4)C_2H_4 + (3/2)CH_4$	−5.8	−4.5
(5) $As_2O_3 + AlMe_3 \rightarrow (1/2)\ Al_2O_3 + (1/2)As_4 + (3/2)C_2H_4 + (3/2)H_2O$	−6.3	−3.1
(6) $4As_2O_3 + AlMe_3 \rightarrow (1/2)Al_2O_3 + 2As_4 + 3CO_2 + (9/2)H_2O$	−15.7	−2.5

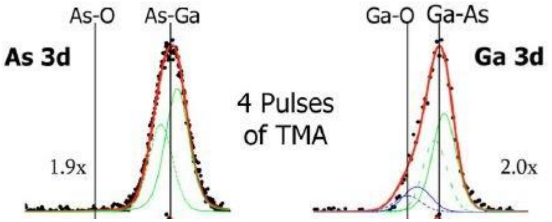


Modeling of the “self-cleaning”: previous study

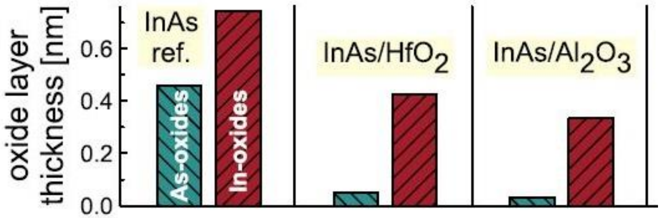


$Al(CH_3)_3$ pulses

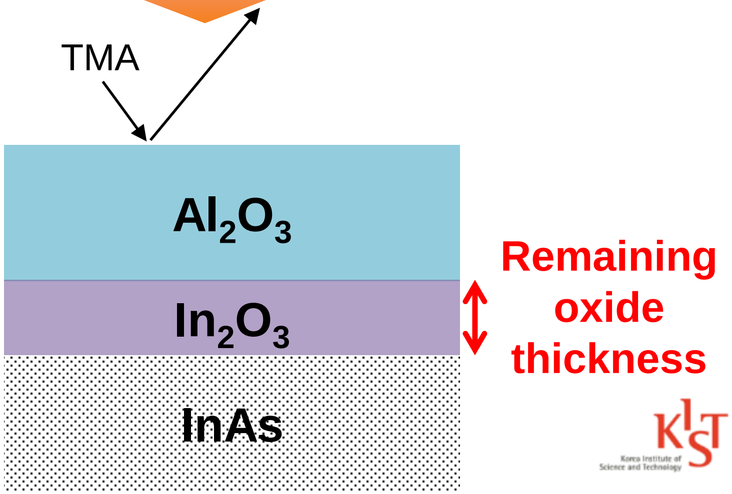
Remaining Ⅲ-oxides



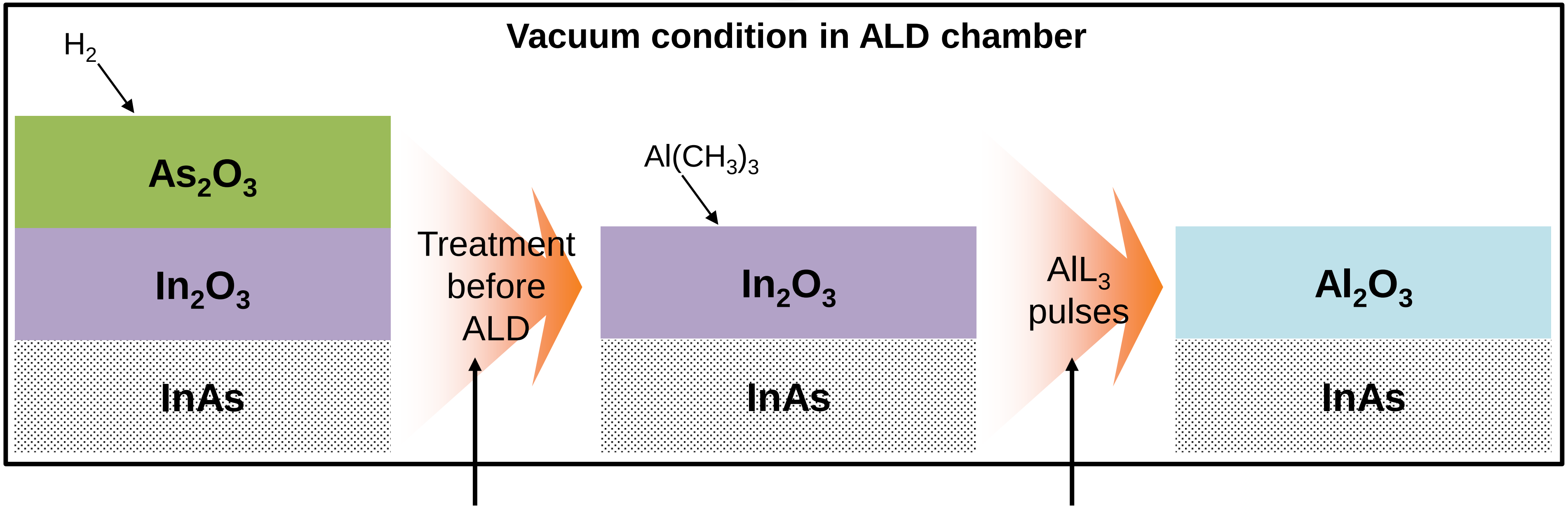
Appl. Phys. Lett. 94, 222108 (2009).



Appl. Phys. Lett. 97, 132904 (2010).



Modeling of the “self-cleaning”: this study



$As_2O_3 + 3H_2 \rightarrow 1/2As_4 + 3H_2O$
or else…

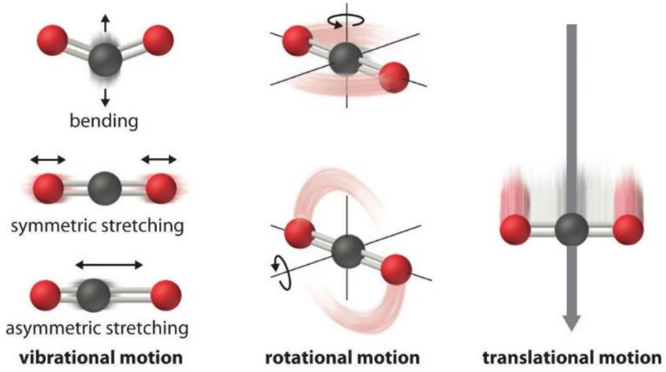
$1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + InMe_3$
or else…

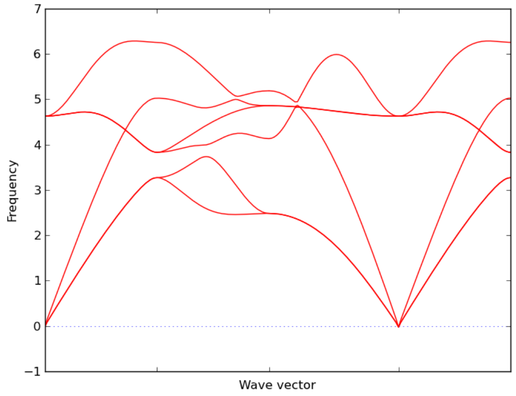
- **Possible reaction? ΔG>0 or ΔG<0**
- **Then how?? Atomic mechanism**

Calculation methods

1. Bulk thermodynamics

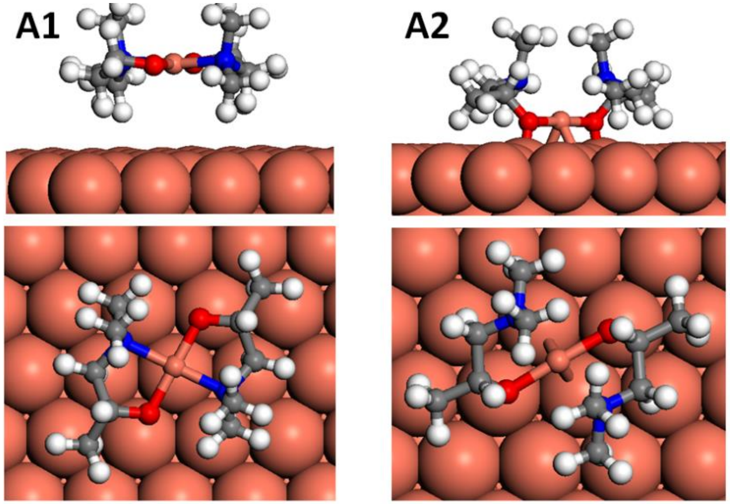
- VASP + PHONOPY
- 500 eV cut-off with PBE functional
- $\mu_{i(gas)}(T,P) = \frac{-k_B T \ln Q_{i(gas)}^{tot} + PV}{N}.$
- $Q_{i(gas)}^{tot} = \frac{1}{N!}(q^{trans} q^{rot} q^{vib} q^{elec})^N$

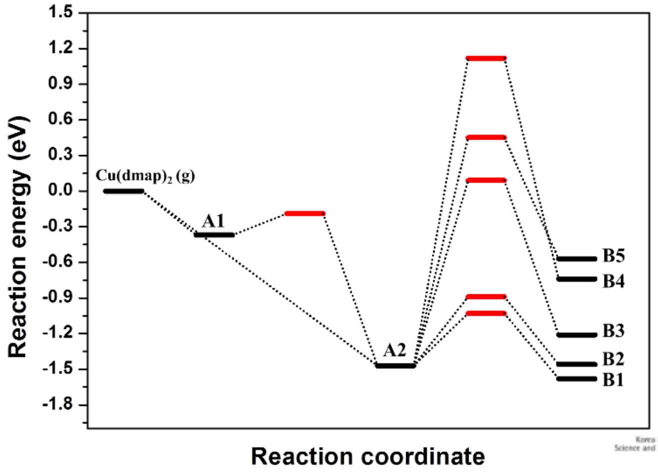




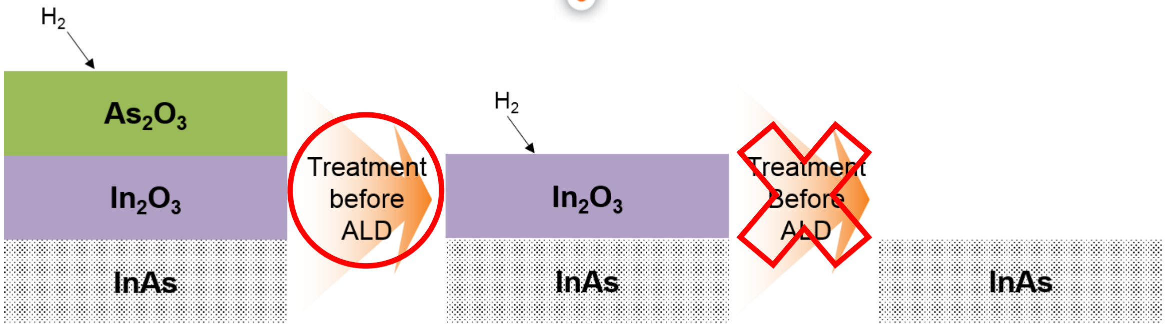
2. Atomic mechanism

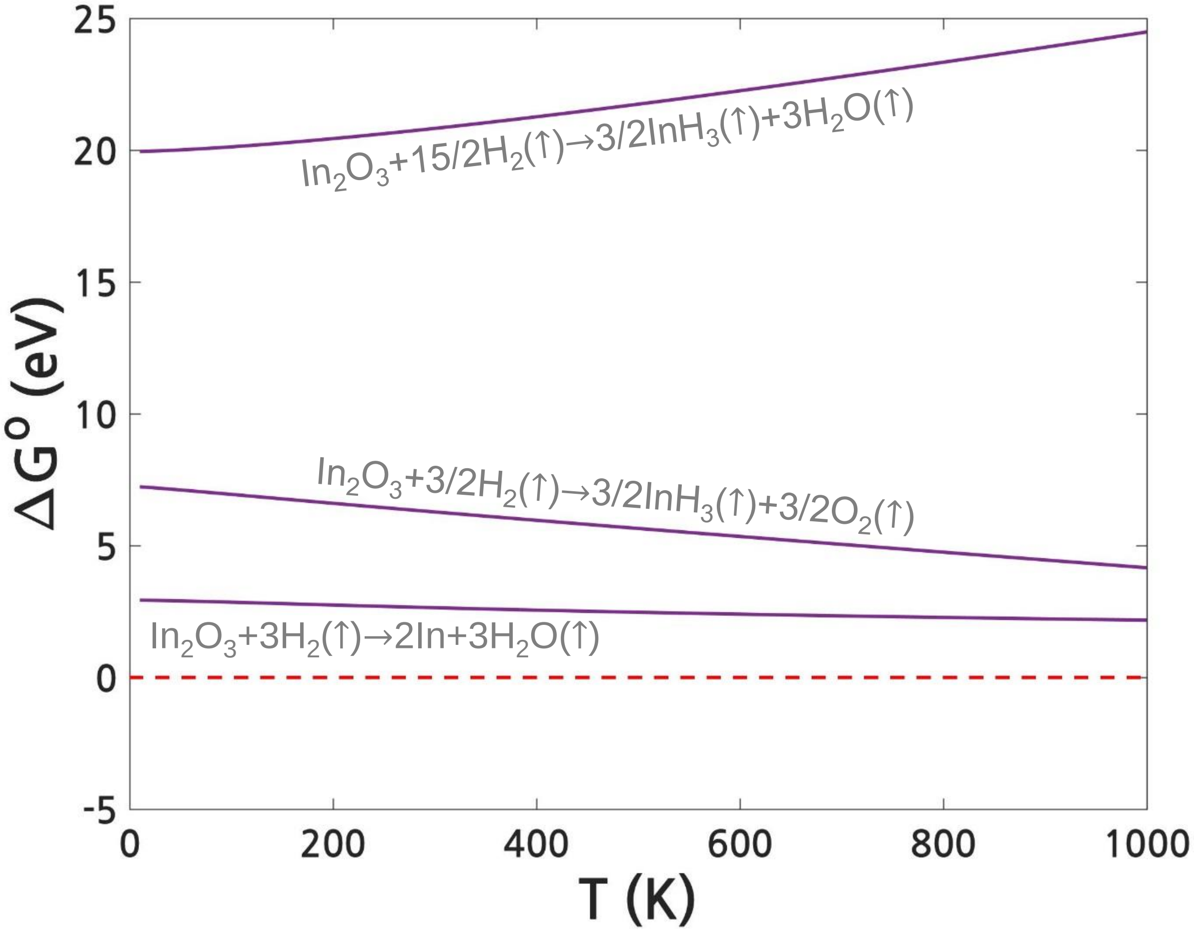
- VASP
- 500 eV cut-off with PBE functional



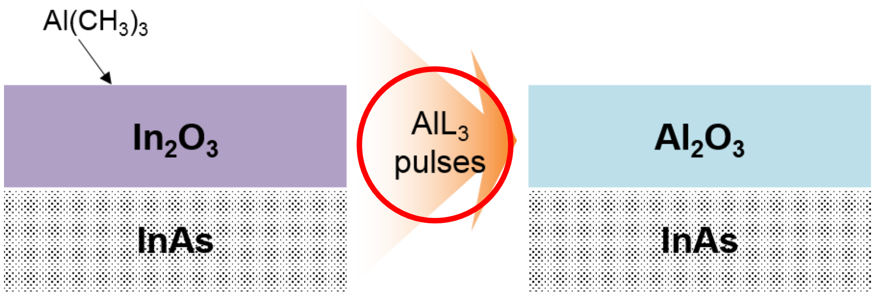


InAs(001) cleaning: H_2 pretreatment



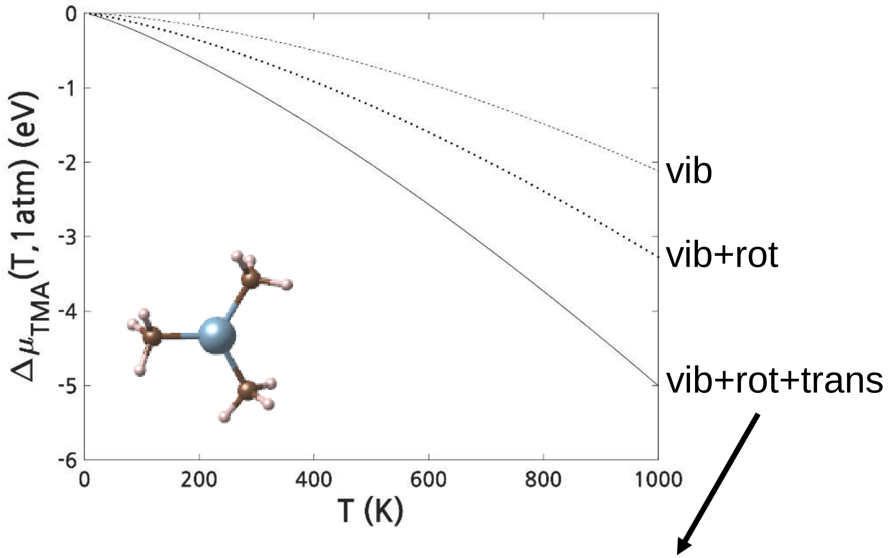


InAs(001) cleaning: AlL$_3$ pulse (L=alkyl)



$1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + InMe_3$

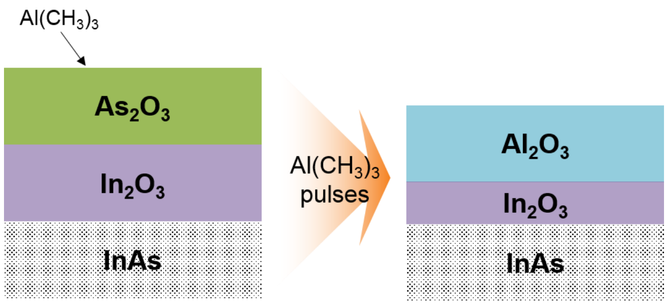
$$\Delta G = \frac{1}{2}\mu_{Al2O3} + \mu_{InMe3} - \frac{1}{2}\mu_{In2O3} - \mu_{AlMe3}$$



$$\mu_{TMA} = E^{0\,K}_{TMA} + ZPE_{TMA} + \Delta\mu^{vib+rot+trans}_{TMA}$$

	Reaction	$\Delta G^{573\ K}$ (eV)
1	$1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + InMe_3$	-2.45
2	$1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + In + 3/2C_2H_6$	-3.88
3	$In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + 2In + 3/2OMe_2$	-1.57
4	$1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + InH_3 + 3/2C_2H_4$	-0.82
5	$1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + In + 3/4C_2H_4 + 3/2CH_4$	-3.89
6	$In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + 2In + 3/2C_2H_4 + 3/2H_2O$	-2.74

InAs(001) cleaning: As_2O_3 vs In_2O_3


$Al(CH_3)_3$

As_2O_3

In_2O_3

InAs

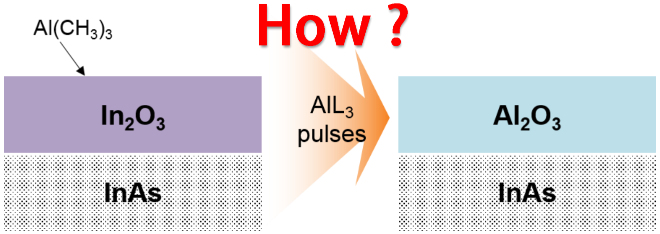
$Al(CH_3)_3$ pulses

Al_2O_3

In_2O_3

InAs

VS


$Al(CH_3)_3$

How ?

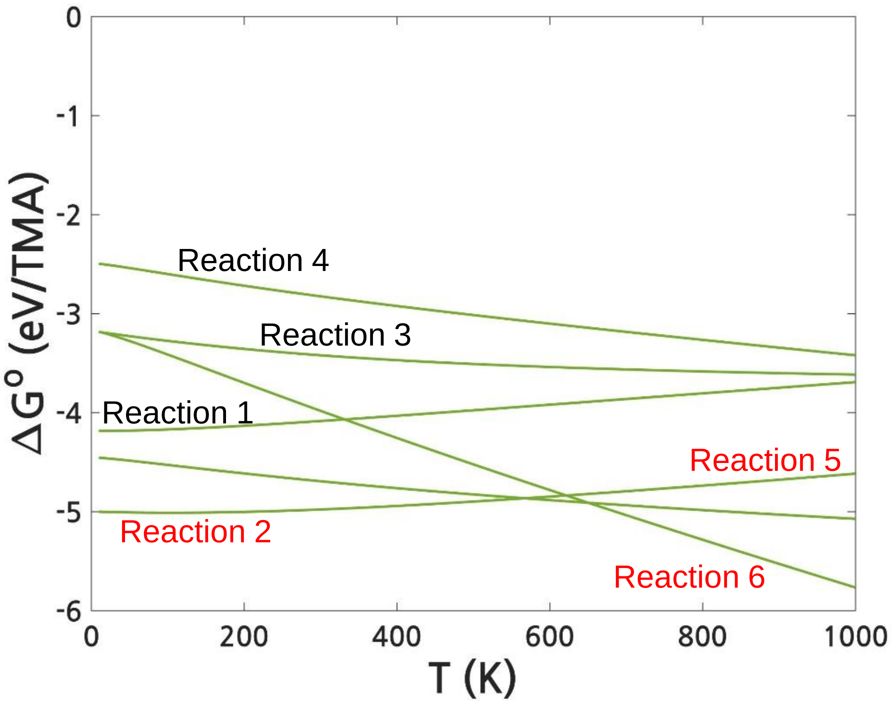
In_2O_3

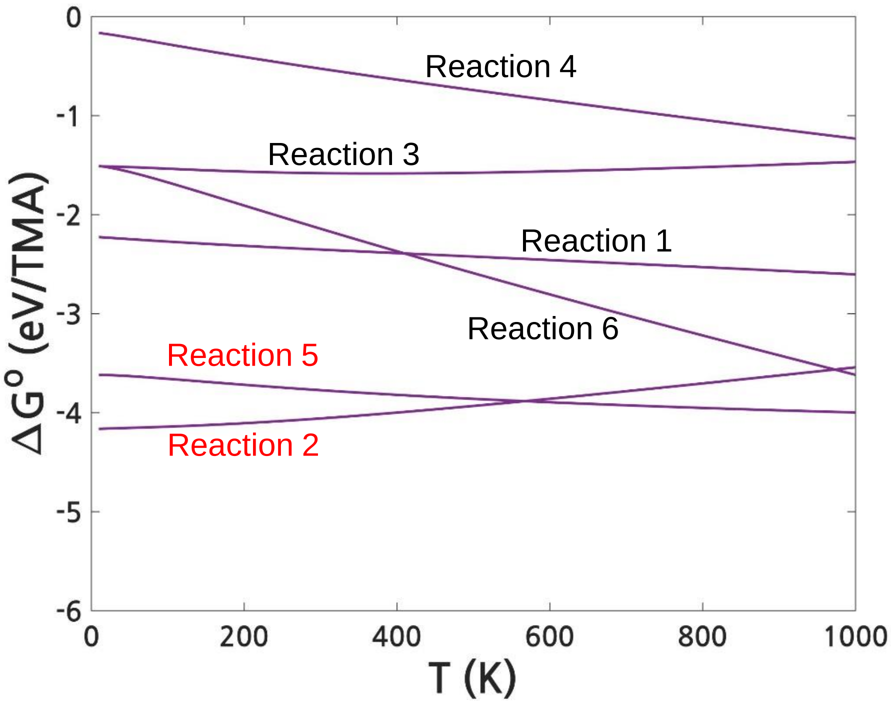
InAs

AlL_3 pulses

Al_2O_3

InAs

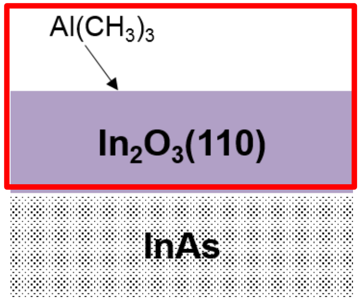


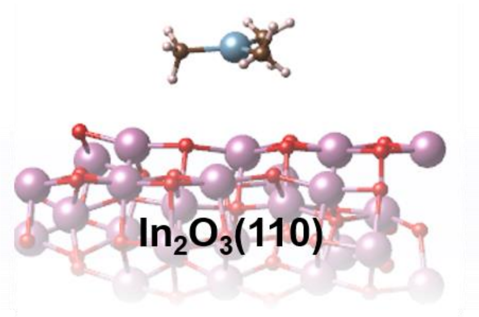


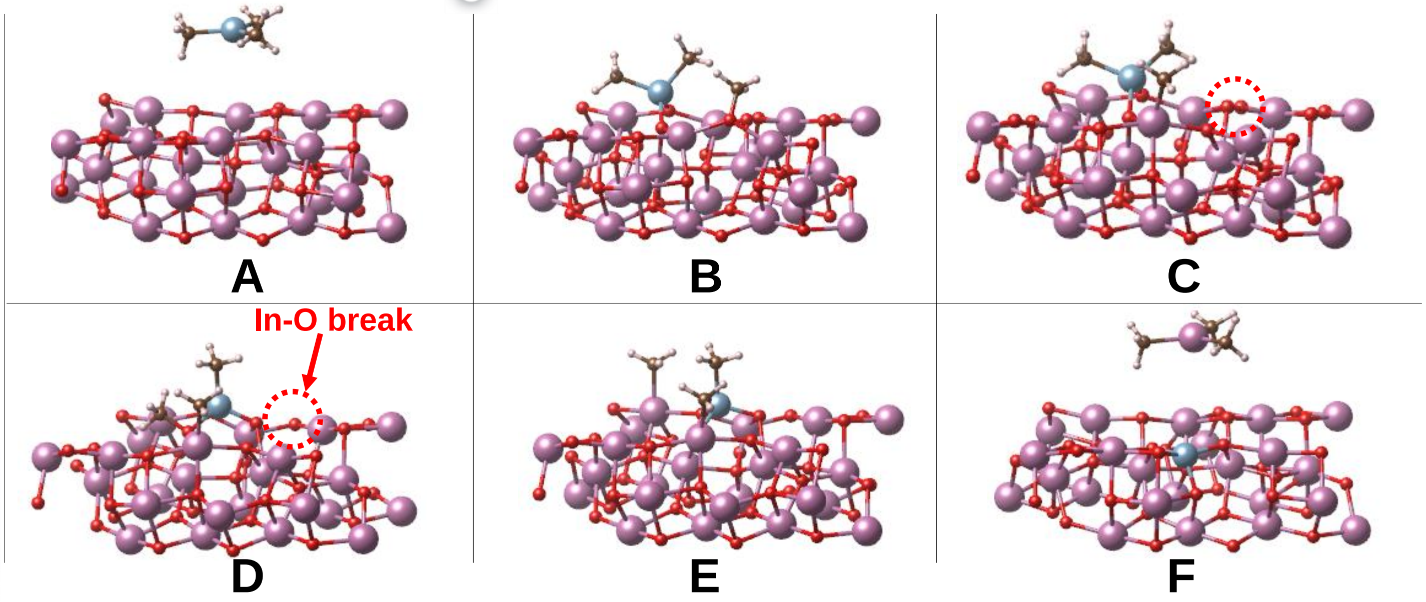
2. $1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + In + 3/2C_2H_6$

5. $1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + In + 3/4C_2H_4 + 3/2CH_4$

Atomic mechanism: L-transfer (L=methyl)

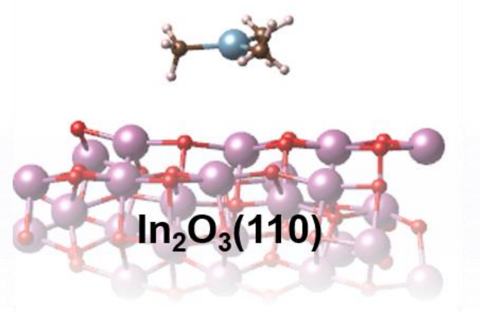




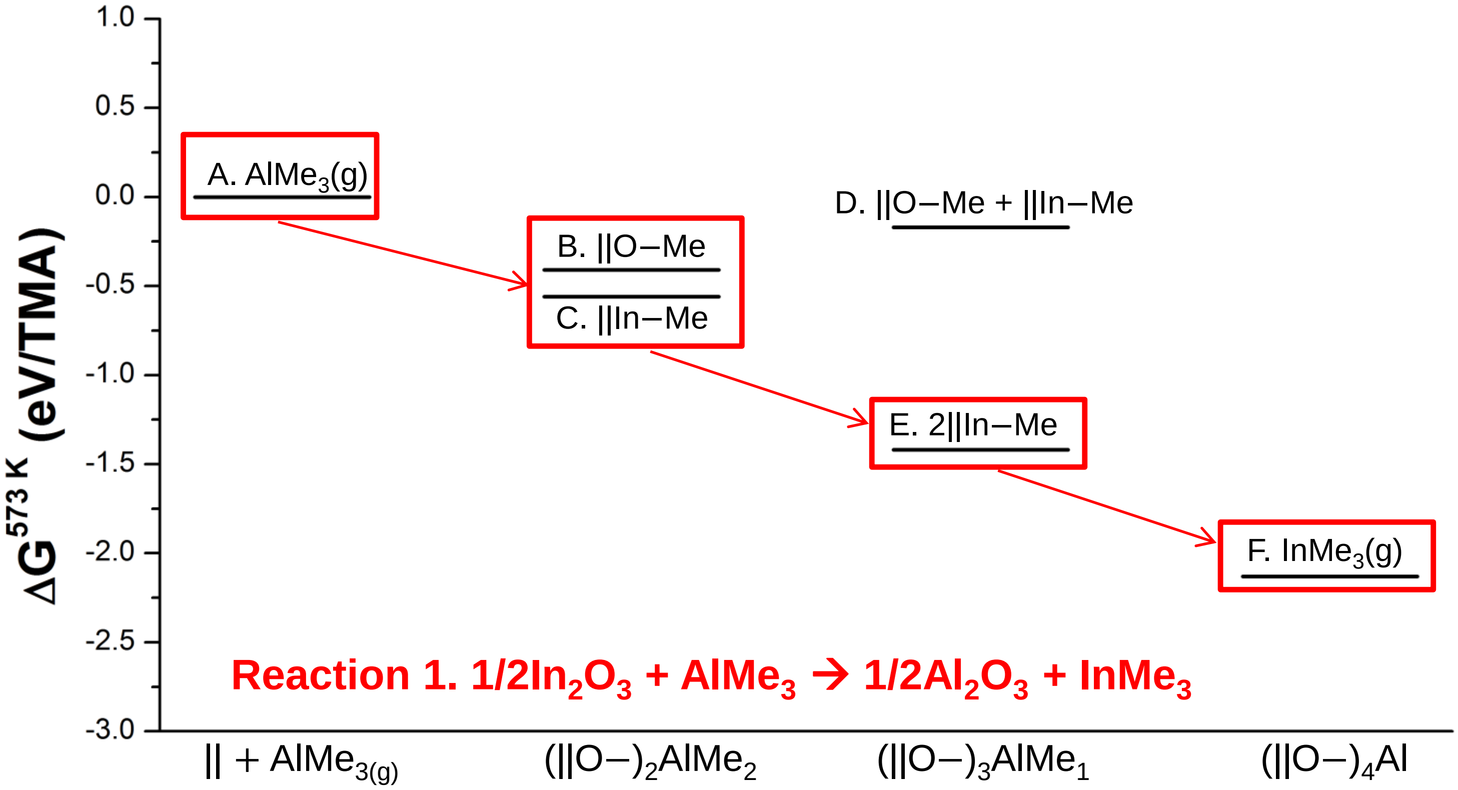


	Products at surface	$\Delta G^{573\,K}$ (eV)
A	In_2O_3(surf) + $AlMe_3$(g)	0.00
B	$(\|\|O-)_2AlMe_2$ + $\|\|O-Me$	-0.41
C	$(\|\|O-)_2AlMe_2$ + $\|\|In-Me$	-0.56
D	$(\|\|O-)_3AlMe$ + $\|\|O-Me$ + $\|\|In-Me$	-0.17
E	$(\|\|O-)_3AlMe$ + 2 $\|\|In-Me$	-1.42
F	$(\|\|O-)_4Al$ + $InMe_3$(g)	-2.13

Atomic mechanism: L-transfer (L=methyl)

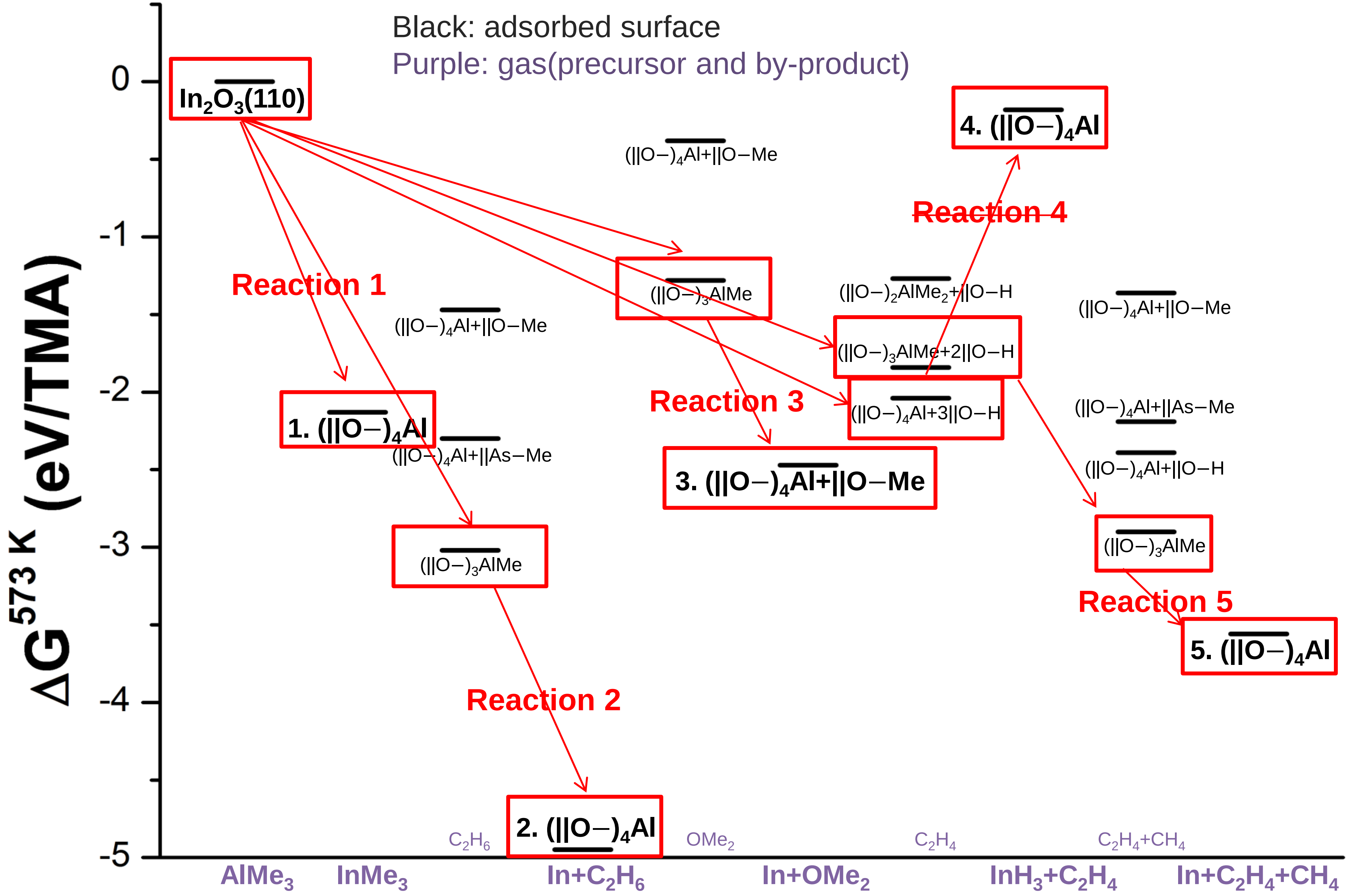


$(||O-)_{1+n}AlMe_{3-n}$ + $n||X-Me$,
where ||X is a binding site of the surface, X=In or O.

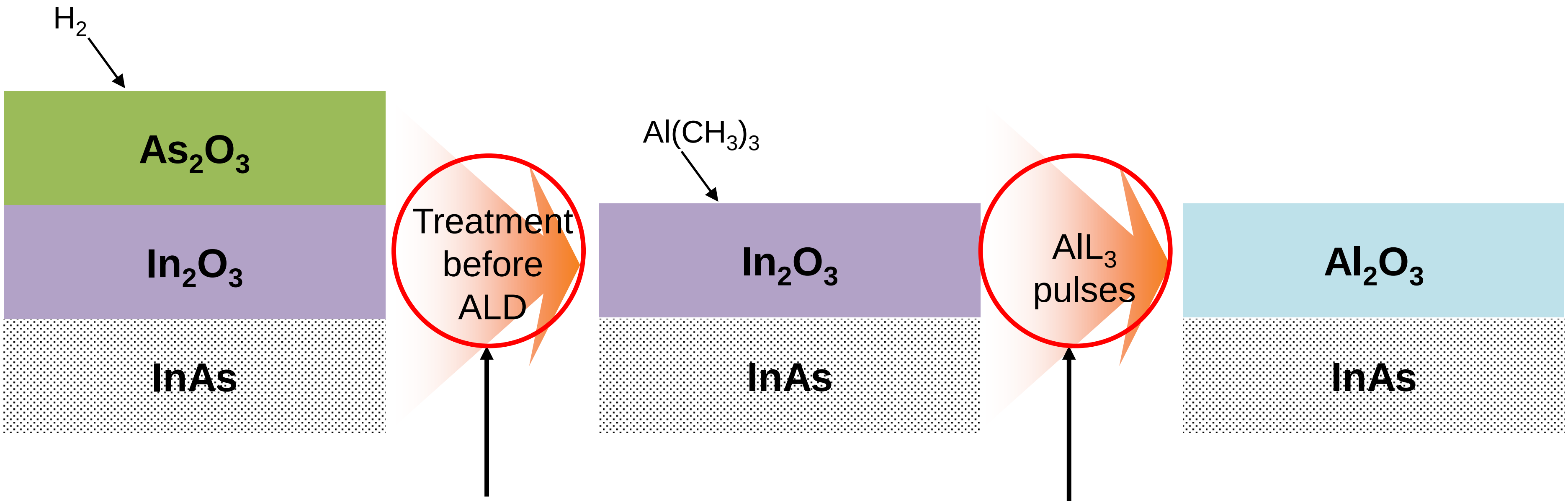


Reaction 1. $1/2In_2O_3 + AlMe_3 \rightarrow 1/2Al_2O_3 + InMe_3$

Atomic mechanism: one TMA on $In_2O_3(110)$



Summary



$As_2O_3 + 3H_2 \rightarrow 1/2As_4(\uparrow) + 3H_2O(\uparrow)$

Most probable path: reaction 2.

$1/2In_2O_3 + AlMe_{3(g)} \rightarrow (||O\text{-})_3AlMe + C_2H_6(\uparrow) \rightarrow (||O\text{-})_4Al + In(\uparrow) + 3/2C_2H_6(\uparrow)$

Inhibited path: reaction 4.

$1/2In_2O_3 + AlMe_{3(g)} \rightarrow (||O\text{-})_4Al + 3||O\text{-}H + 3/2C_2H_4(\uparrow) \rightarrow (||O\text{-})_4Al + InH_3(\uparrow) + 3/2C_2H_4(\uparrow)$