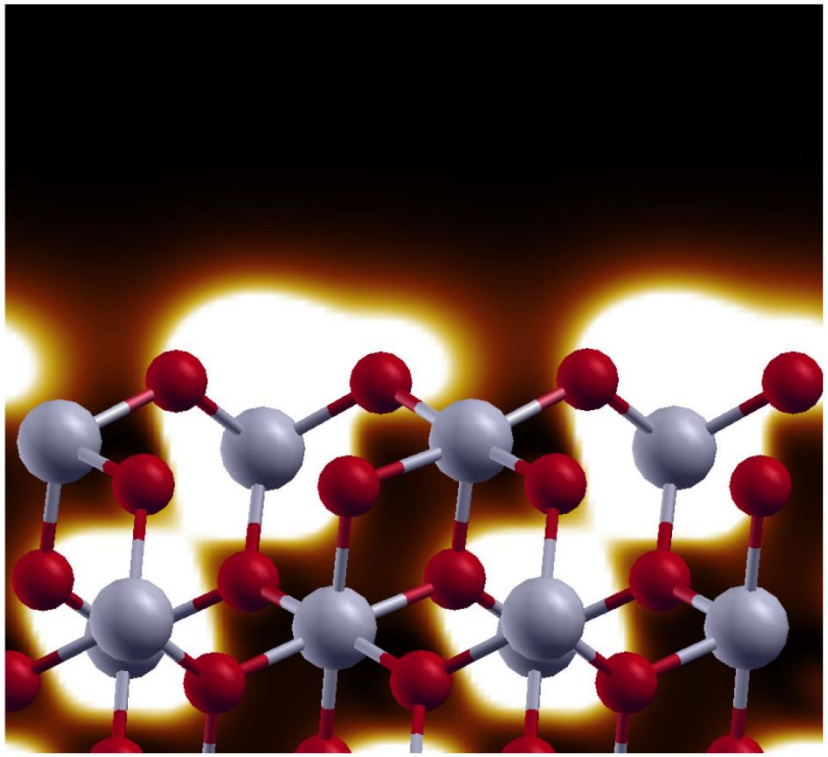
Point defects and surfaces of transparent electrodes studied by DFT-calculations



*Peter Agoston[1], Paul Erhart[1], Andreas Klein[2], Manuel Diehm[1], Arno Fey[1], **Karsten Albe[1]***

TU Darmstadt
[1]FG Materialmodellierung
[2]FG Oberflächenforschung
FB Material- und Geowissenschaften

SFB 595
Deutsche Forschungsgemeinschaft
DFG

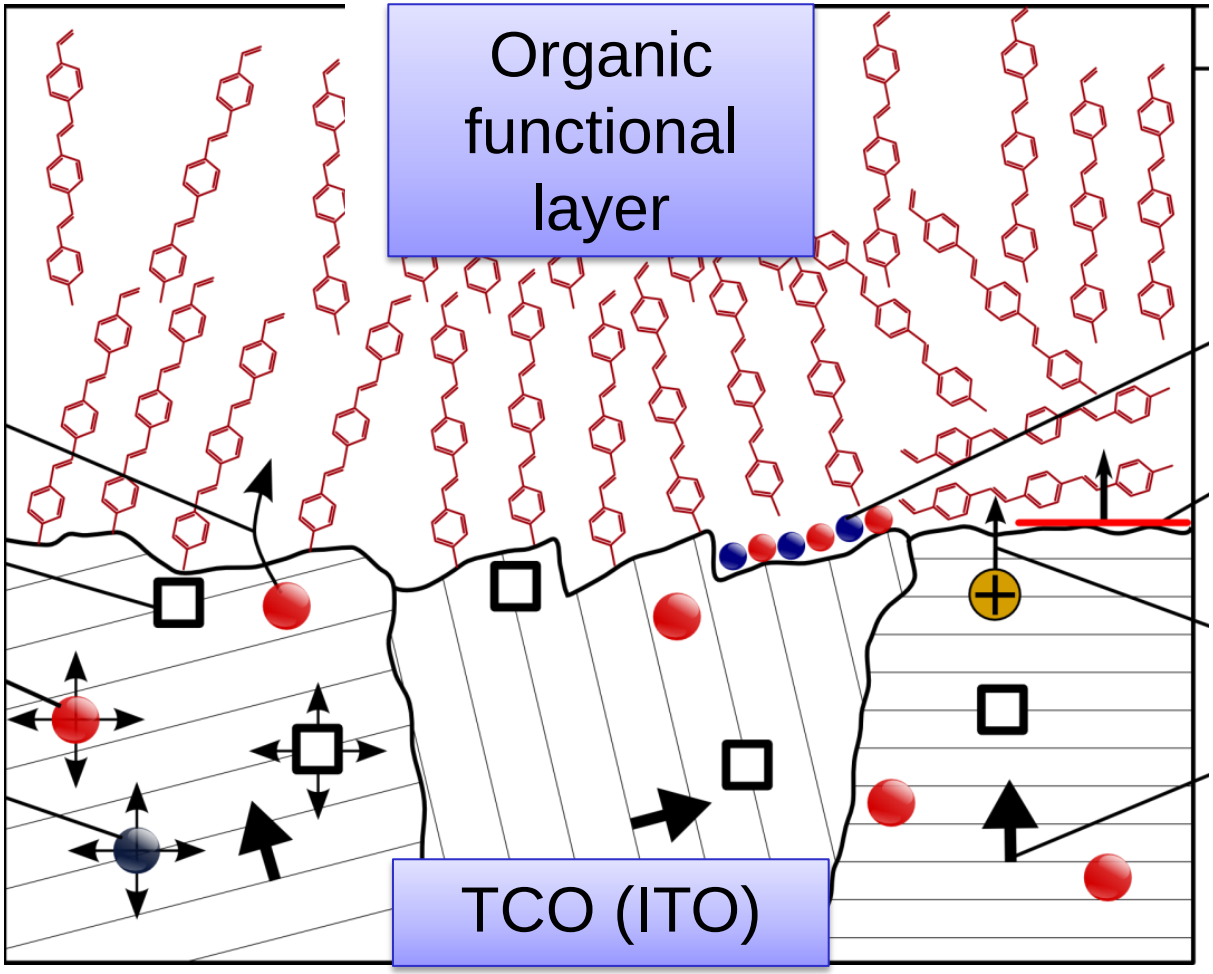
OLEDs and TCOs: Open Questions

TECHNISCHE UNIVERSITÄT DARMSTADT

Exchange Kinetics ?

Point Defects ?

Mobility of Defects and Dopands?



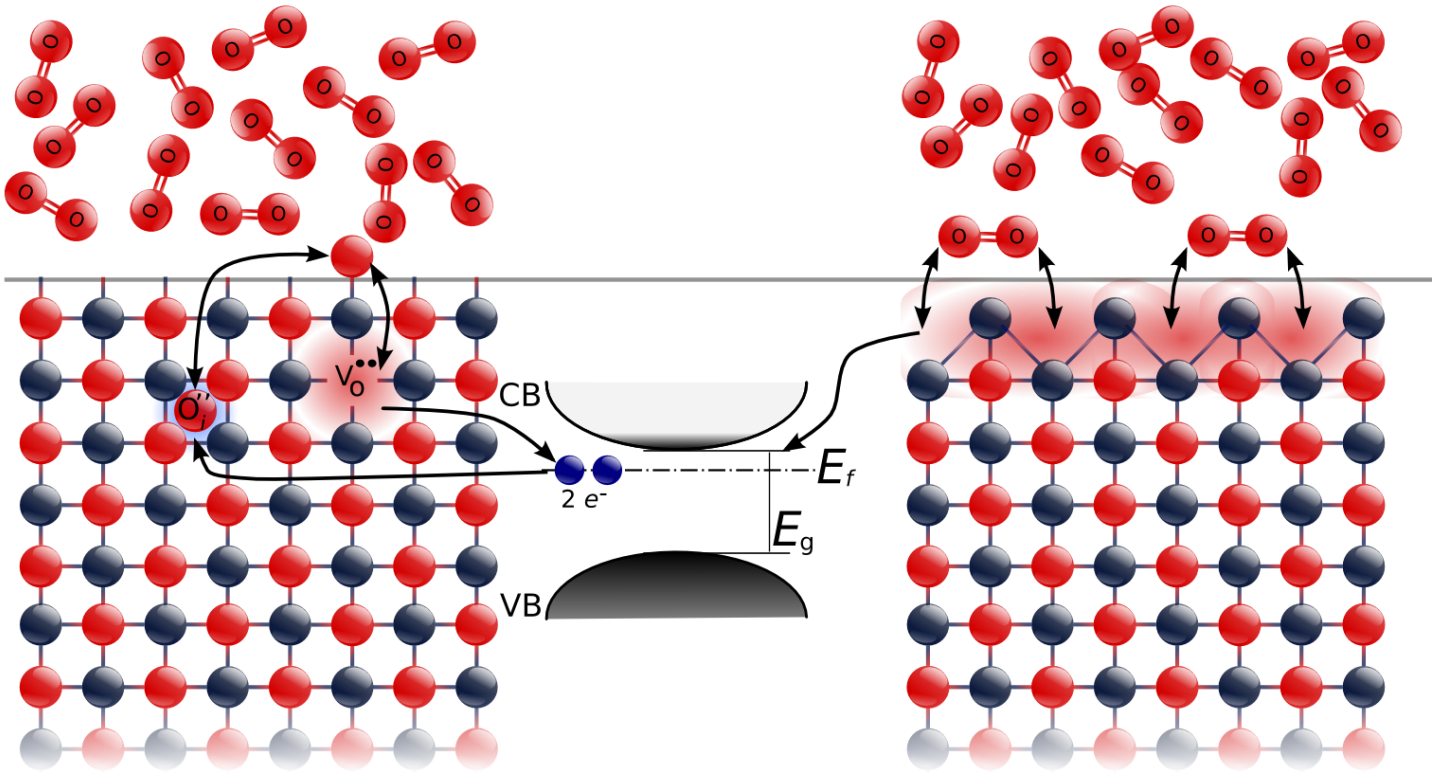
Surface/ Interface Properties ?

Work Function ?

Defect Thermodynamics

TECHNISCHE UNIVERSITÄT DARMSTADT

$$\mu^{o}(p_{O_2},T) = \frac{1}{2}\mu^{\ominus}_{O_2}(p^{\ominus}_{O_2},T) + \frac{1}{2}RT\ln\left(\frac{p_{O_2}}{p^{\ominus}_{O_2}}\right)$$



Defects

Surfaces

$$\gamma = (E_{slab} - TS_{slab} - \sum \mu_i n_i)/2A$$

Surface Stresses and Surface Energies

TECHNISCHE UNIVERSITÄT DARMSTADT

$$G = G_0 + \gamma A$$

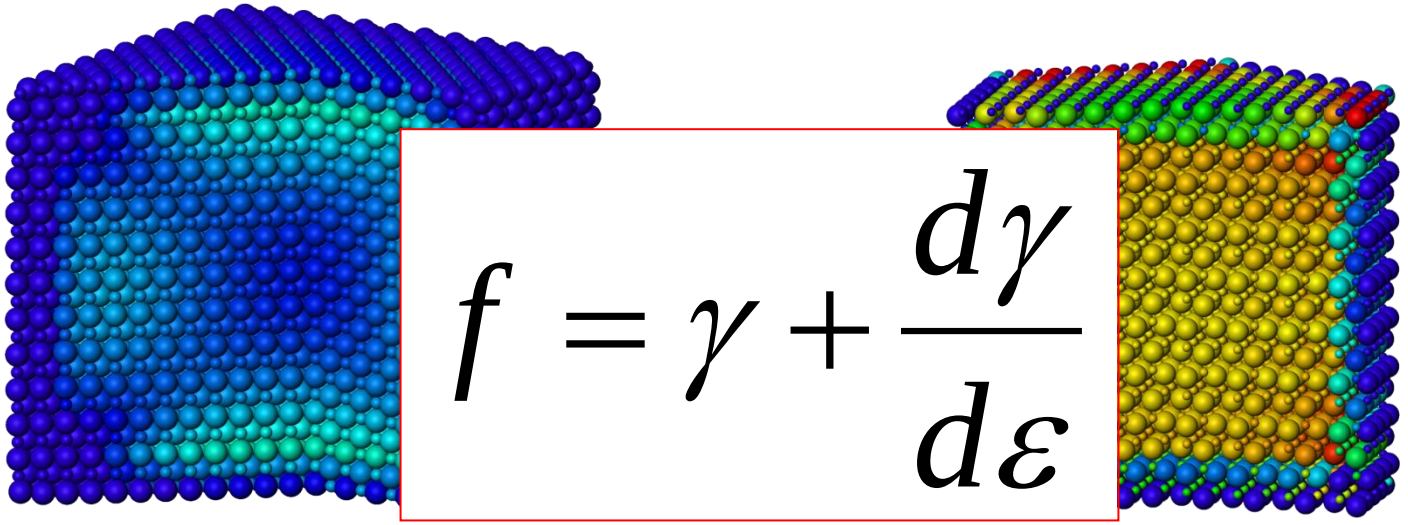
$$dG = d(\gamma A) = \gamma dA + A d\gamma$$

$$= \left(\gamma + A \left(\frac{\partial \gamma}{\partial A} \right) \right) dA$$

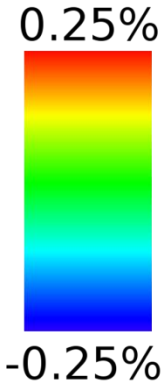
Role of Surface Stresses

TECHNISCHE UNIVERSITÄT DARMSTADT

- MgO (compressive): GaN (tensile)



$$f = \gamma + \frac{d\gamma}{d\varepsilon}$$

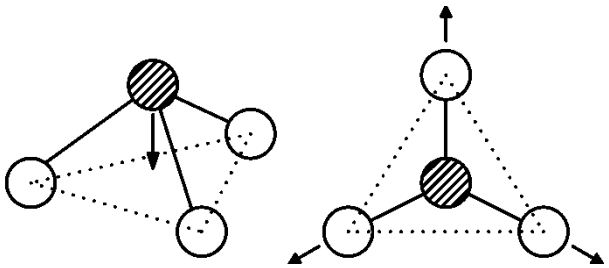


CHEMPHYSCHEM MINIREVIEWS

DOI: 10.1002/cphc.201200257

Size-Dependent Lattice Expansion in Nanoparticles: Reality or Anomaly?

P. Manuel Diehm,* Péter Ágoston, and Karsten Albe[a]



Calculated Surface Stresses (DFT)

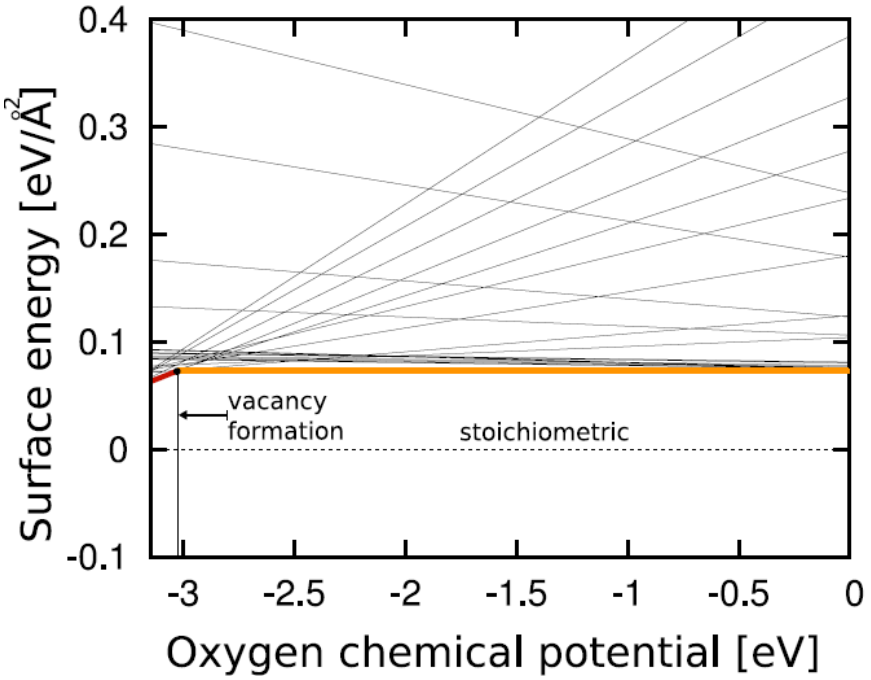
TECHNISCHE UNIVERSITÄT DARMSTADT

Material	Surface	Condition	x-direction	y-direction	γ	f_x	f_y
					(eV Å^{-2})		
hex-Si	(0001)		$\langle 1\bar{1}00 \rangle$	$\langle 1\bar{2}10 \rangle$	0.114	-0.045	-0.039
	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.086	-0.065	-0.032
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.097	-0.043	-0.030
hex-C	(0001)		$\langle 1\bar{1}00 \rangle$	$\langle 1\bar{2}10 \rangle$	0.419	0.003	0.029
	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.184	-0.160	0.056
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.227	-0.337	0.020
GaN	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.125	-0.106	-0.055
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.133	-0.031	-0.030
ZnO	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.075	-0.088	-0.059
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.079	-0.011	-0.038
BeO	$(1\bar{1}00)$		$\langle 1\bar{2}10 \rangle$	$\langle 0001 \rangle$	0.109	-0.089	-0.054
	$(1\bar{2}10)$		$\langle 1\bar{1}00 \rangle$	$\langle 0001 \rangle$	0.113	-0.039	-0.044
MgO	(001)		$\langle 100 \rangle$	$\langle 100 \rangle$	0.073	0.223	0.223
CdO	(001)		$\langle 100 \rangle$	$\langle 100 \rangle$	0.051	0.210	0.210
KF	(001)		$\langle 100 \rangle$	$\langle 100 \rangle$	0.016	0.037	0.037
CsF	(001)		$\langle 100 \rangle$	$\langle 100 \rangle$	0.011	0.033	0.033
CsCl	(110)		$\langle 110 \rangle$	$\langle 100 \rangle$	0.014	0.058	-0.002
c-$SrTiO_3$	(001)	SrO-termination	$\langle 100 \rangle$	$\langle 100 \rangle$	0.166	0.116	0.116

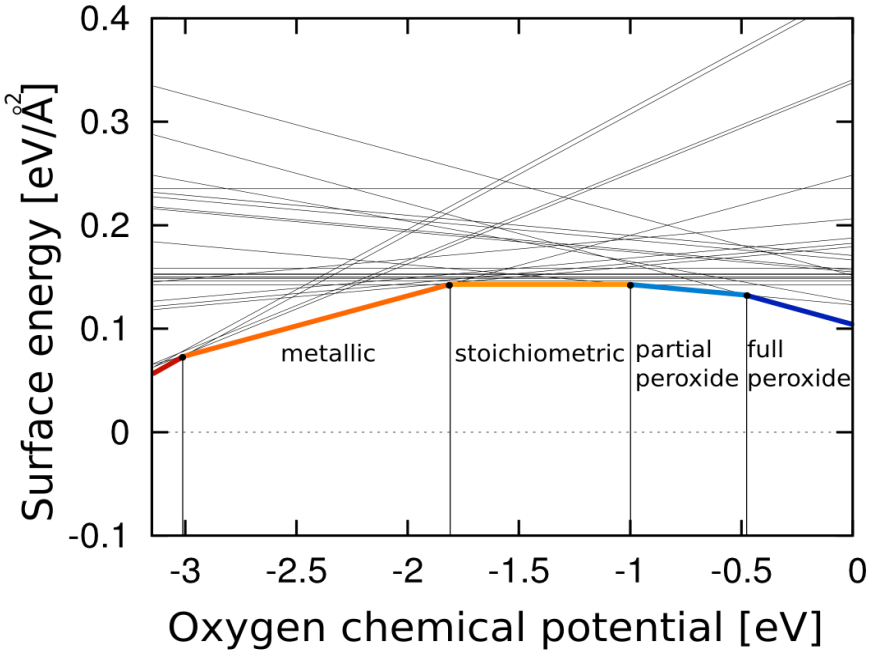
In_2O_3: (111) vs. (001) surfaces

TECHNISCHE UNIVERSITÄT DARMSTADT

non-polar (type-II)



polar (type-IIIa)

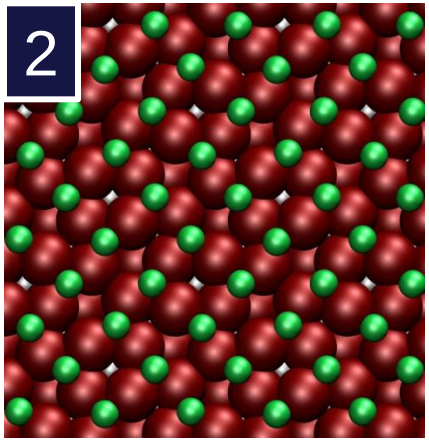


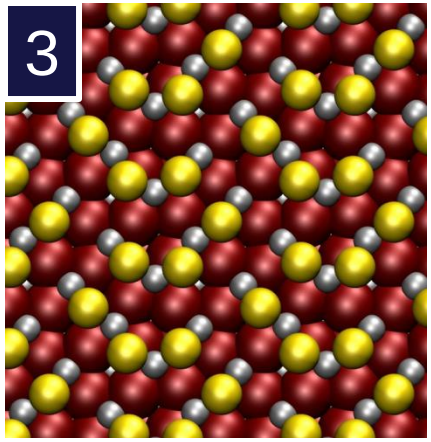
- (111) mainly stoichiometric
- Several phase transitions in the case of (001)

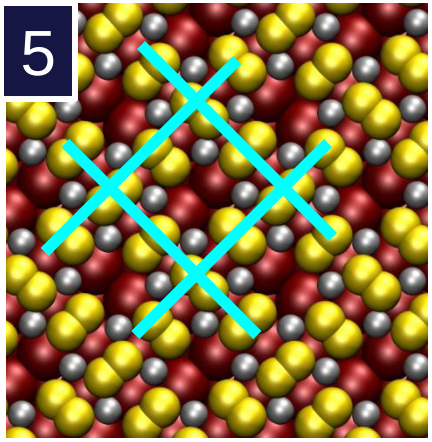
ITO-(001)

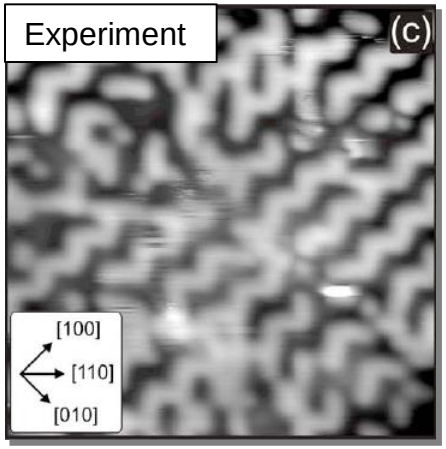
Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

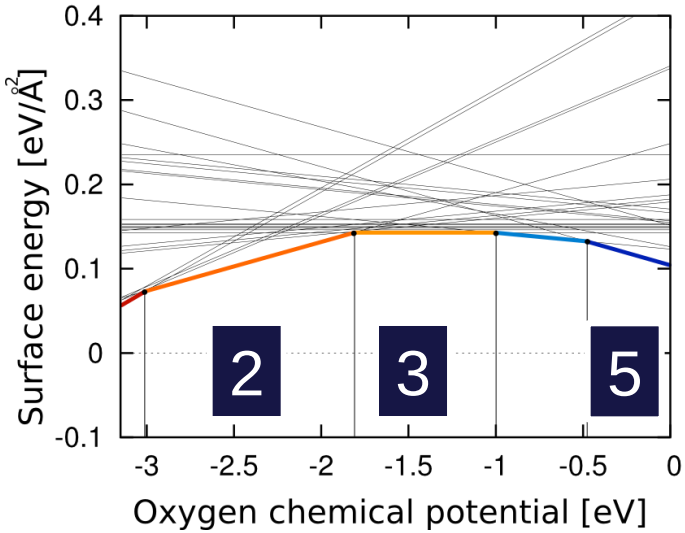
TECHNISCHE UNIVERSITÄT DARMSTADT

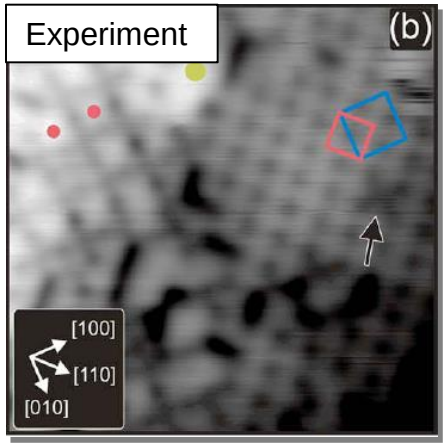










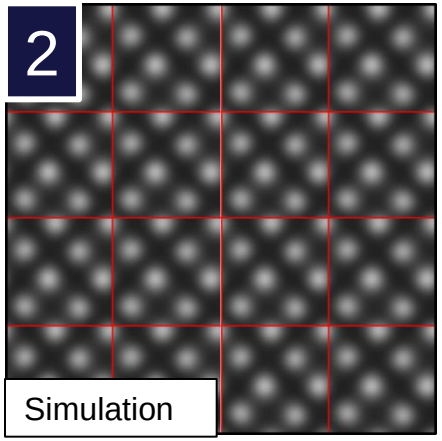


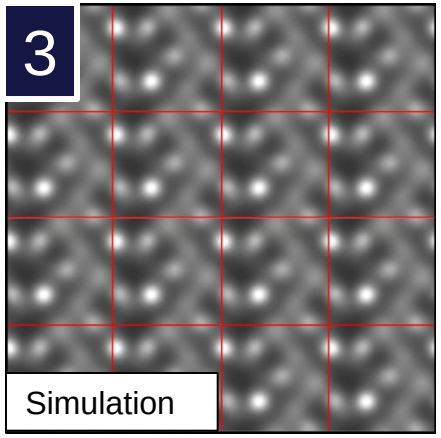
E. Morales, U. Diebold, Appl. Phys. Lett. , **139**, 665-672 (2009)

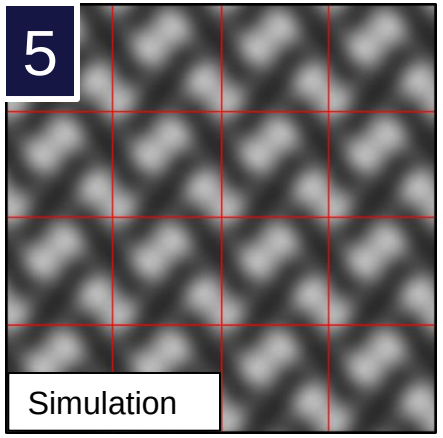
In_2O_3-(001)

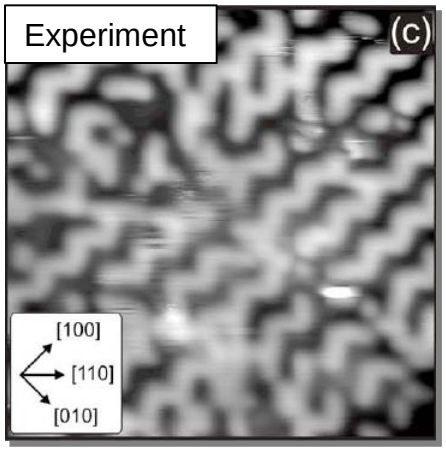
Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

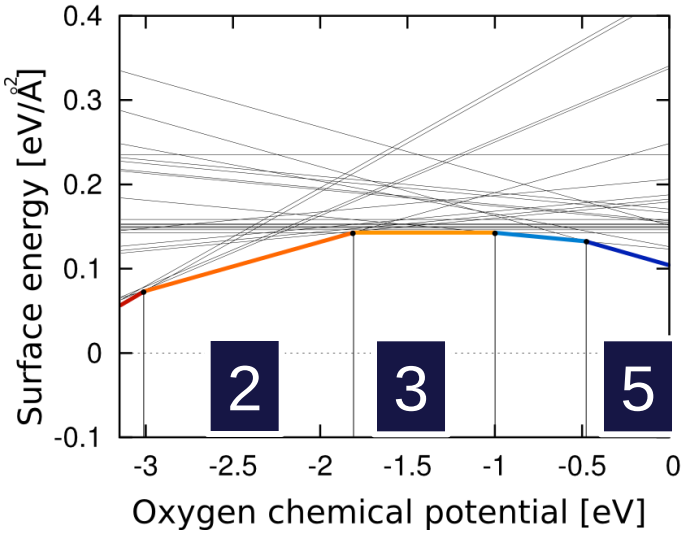
TECHNISCHE UNIVERSITÄT DARMSTADT

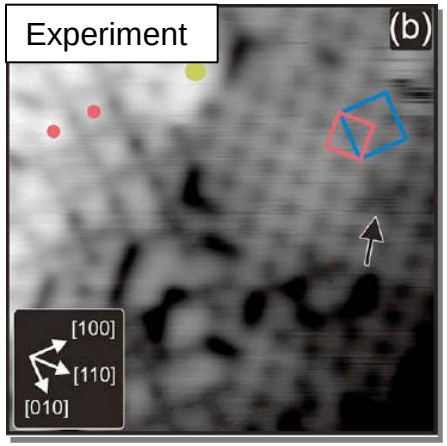










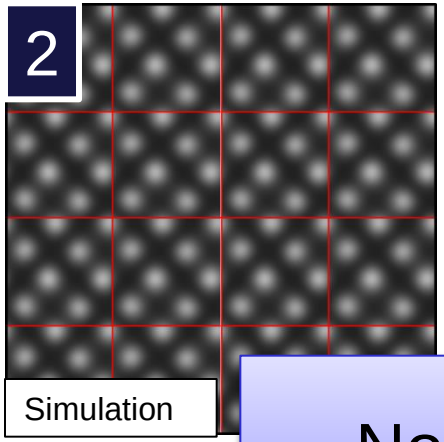


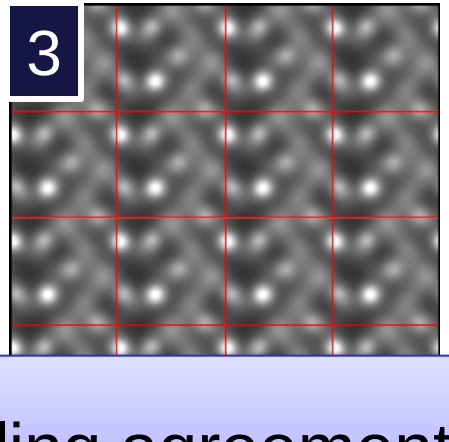
E. Morales, U. Diebold, Appl. Phys. Lett. , **139**, 665-672 (2009)

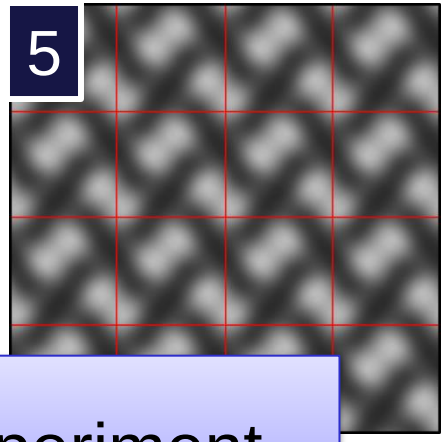
In_2O_3-(001)

Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

TECHNISCHE UNIVERSITÄT DARMSTADT



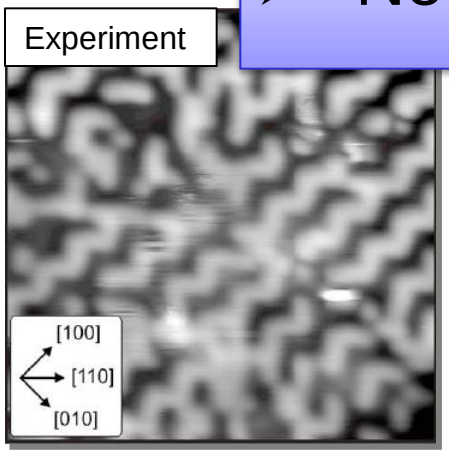


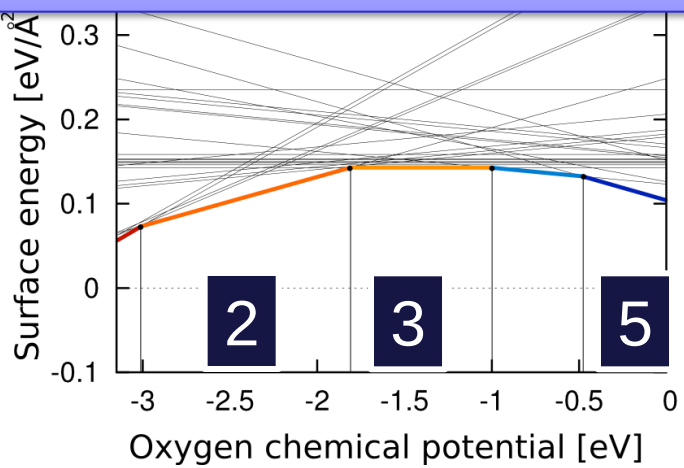


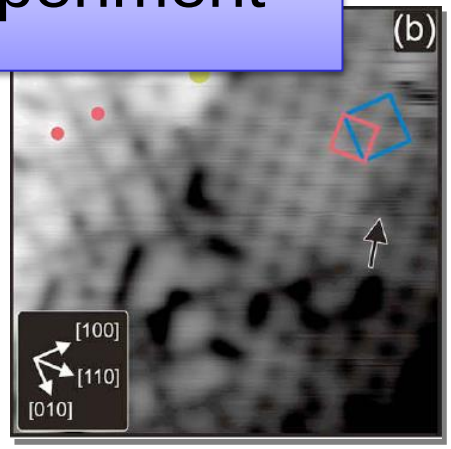
Simulation

Experiment

- No compelling agreement with experiment







E. Morales, U. Diebold, Appl. Phys. Lett. , **139**, 665-672 (2009)

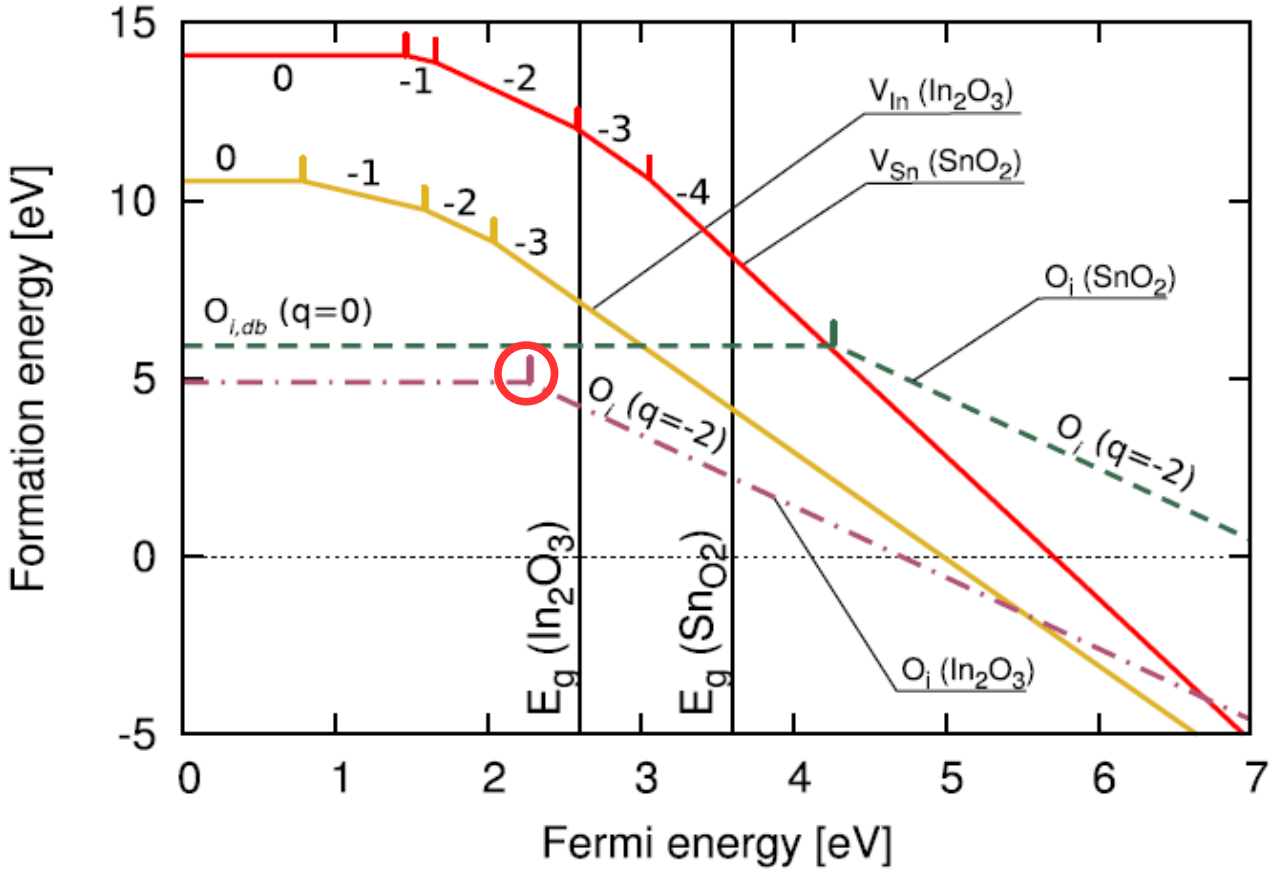
E
T
T


LIEBLING, ICH HAB ÜBER UNS NACH-GEDACHT...
WOMIT DENN?
WWW.DER-FLIX.DE

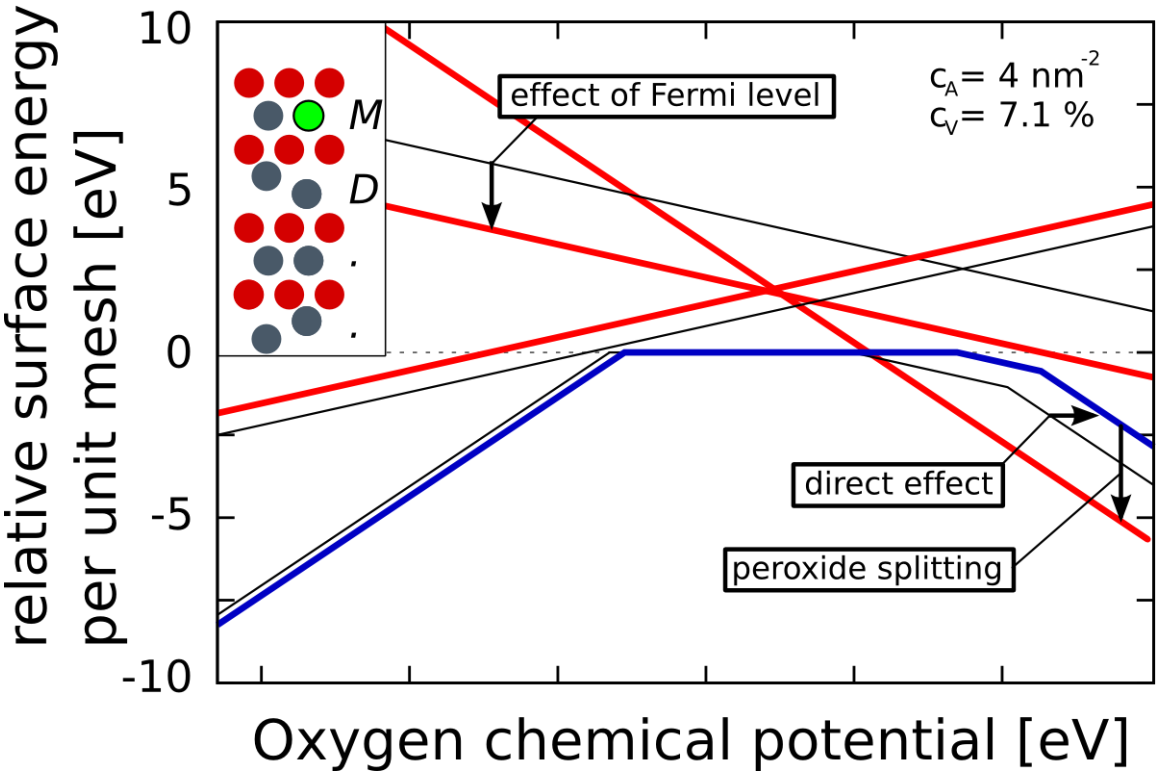
Doping effect at In_2O_3-(001) ?

TECHNISCHE UNIVERSITÄT DARMSTADT

$$O_2 + 2e^- \rightleftharpoons O^{2-}_{2,surf}$$



Doping effect

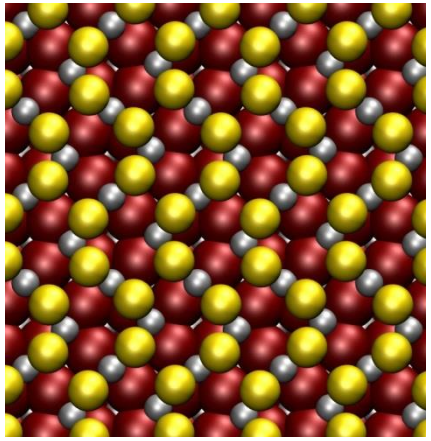


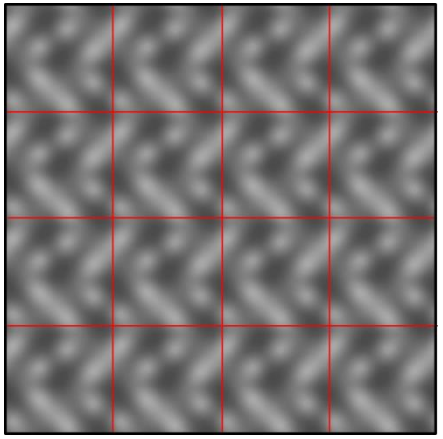
- Peroxide splitting highly favorable

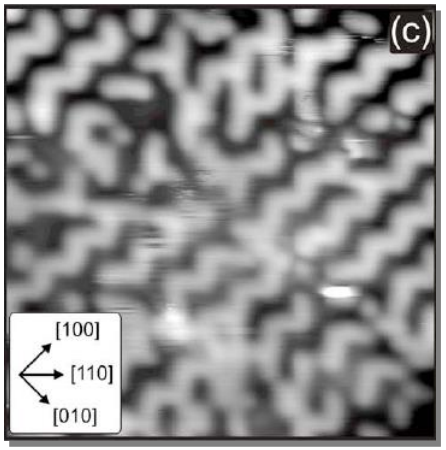
ITO-(001)

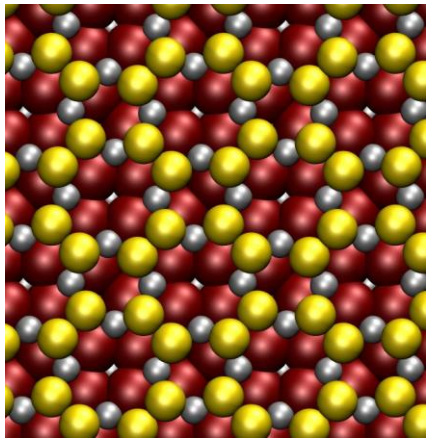
Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

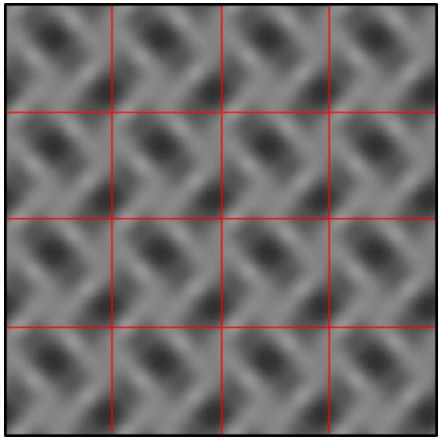
TECHNISCHE UNIVERSITÄT DARMSTADT

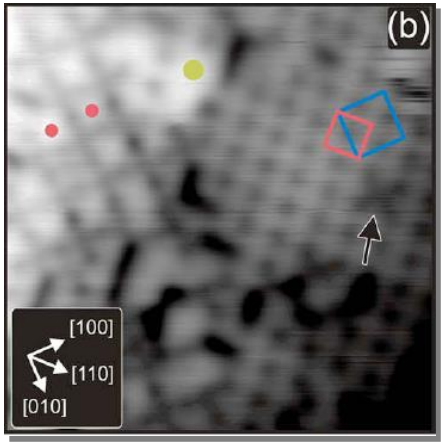












E. Morales, U. Diebold, Appl. Phys. Lett. , **139**, 665-672 (2009)

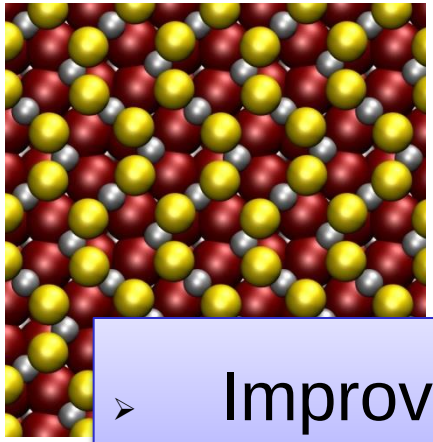
Simulation

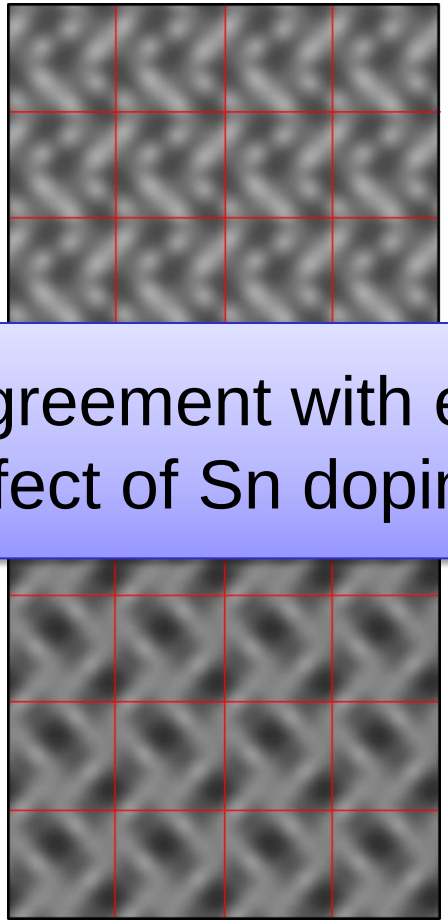
Experiment

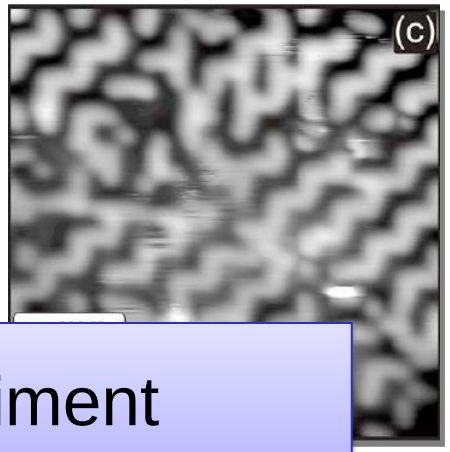
ITO-(001)

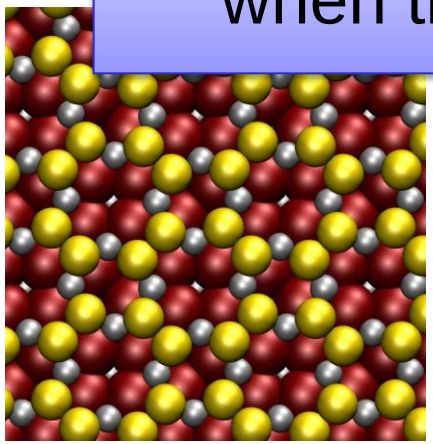
Oxygen : Indium :
Oxygen (1. layer) : Indium (1. layer) :

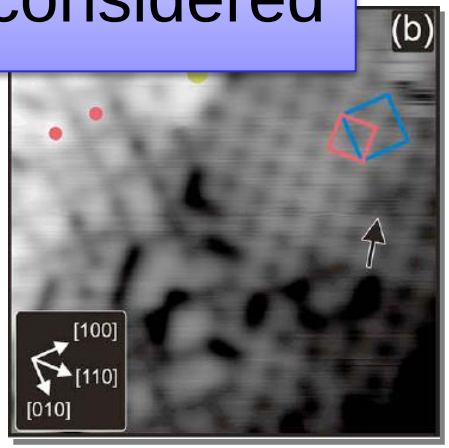
TECHNISCHE UNIVERSITÄT DARMSTADT





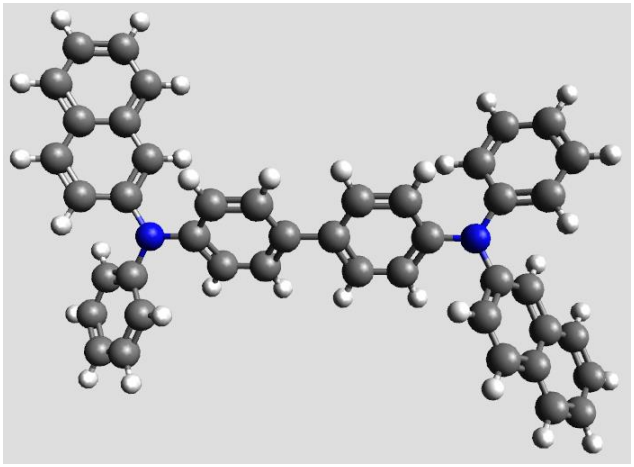




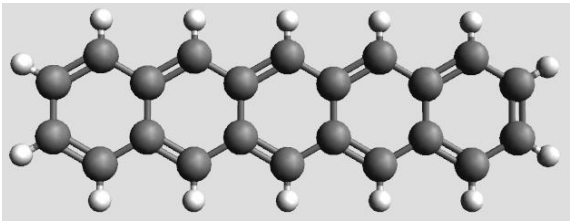


- Improved agreement with experiment when the effect of Sn doping is considered

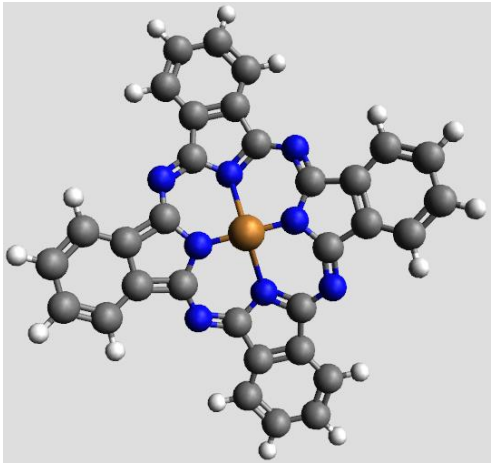
Organic: small molecules (SM) as HTL



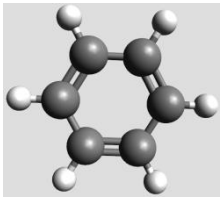
α-NPD
(N,N′-di(1-naphthyl)-N,N′-diphenylbenzidine)



Pentacene



CuPC
(copper phthalocyanine)

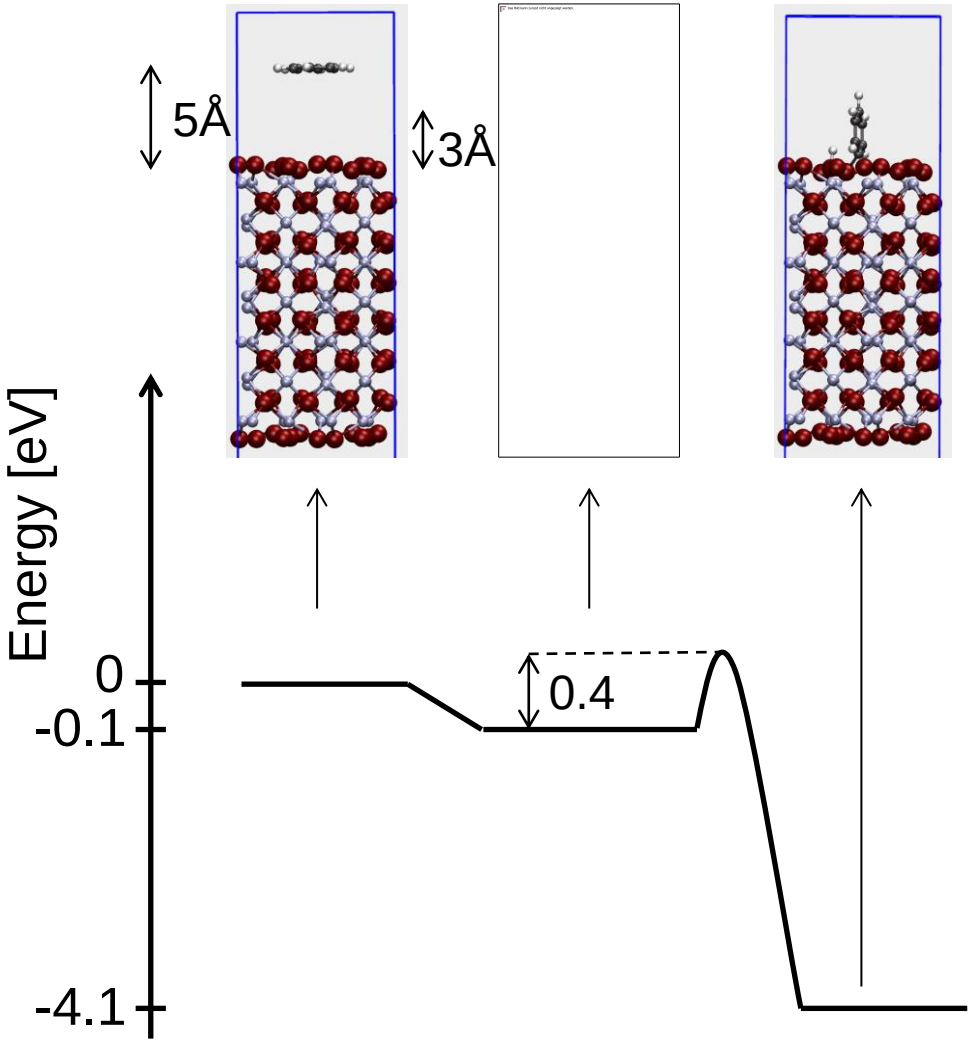


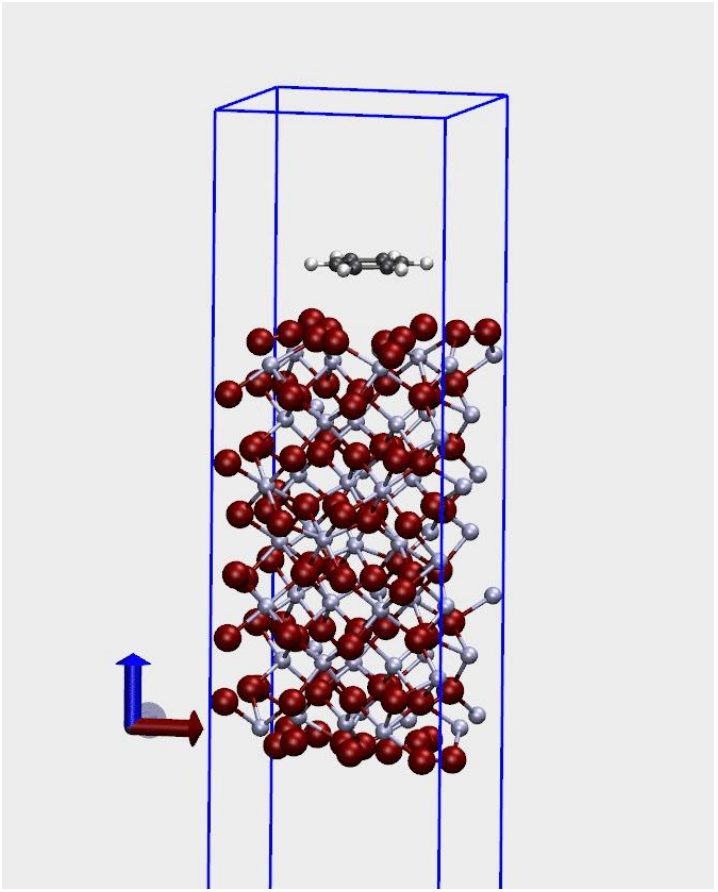
Benzene

- Carbon
- Hydrogen
- Copper
- Nitrogen

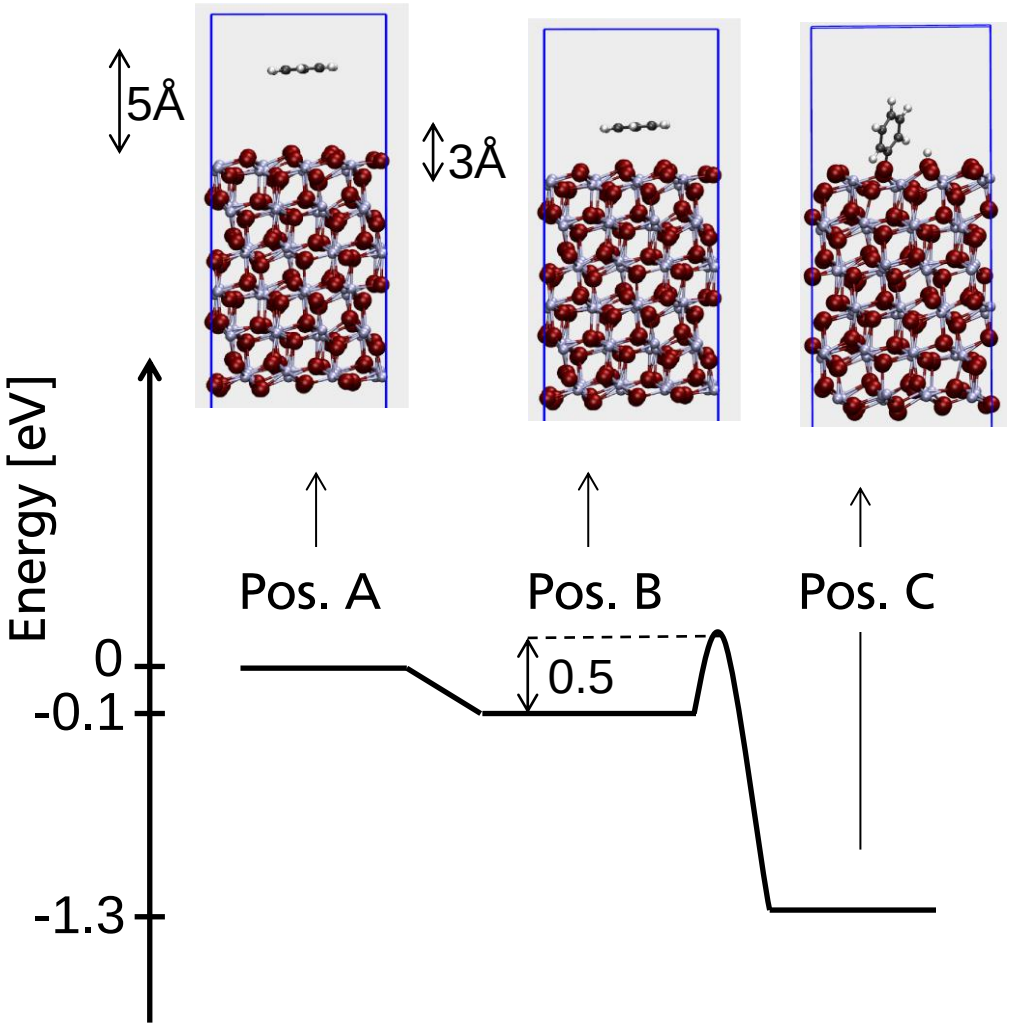
Kinetic barrier on In_2O_3-(100) peroxide surface

TECHNISCHE UNIVERSITÄT DARMSTADT





In_2O_3-(111) surface

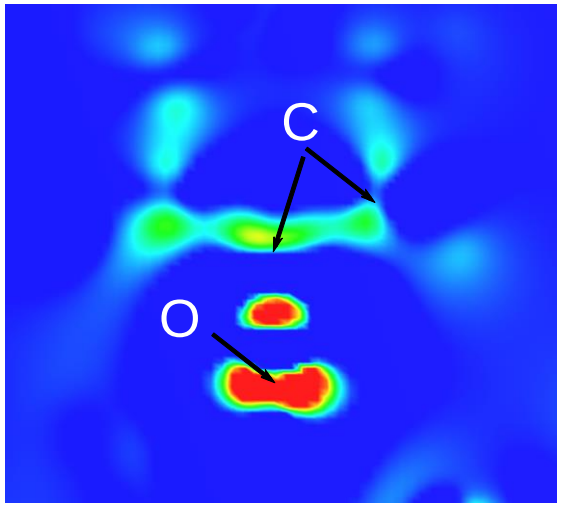


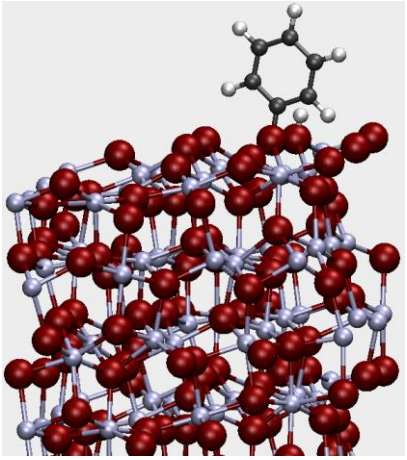
	(100)	(111)
Pos. A	0	0
Pos. B	-0.1	-0.1
Pos. C	-4.1	-1.3
barrier	0.4	0.5

Nature of bonding

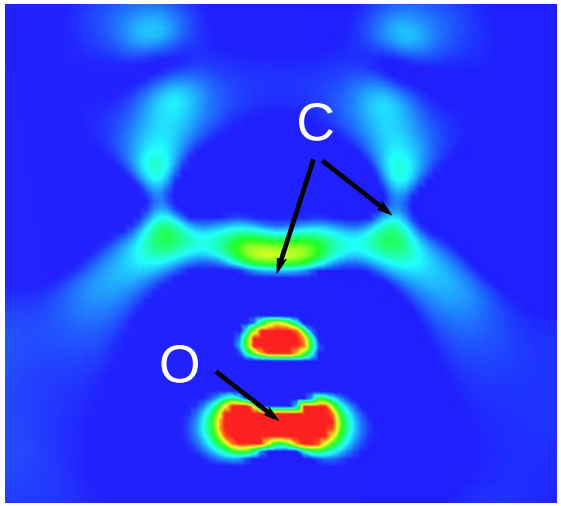
TECHNISCHE UNIVERSITÄT DARMSTADT

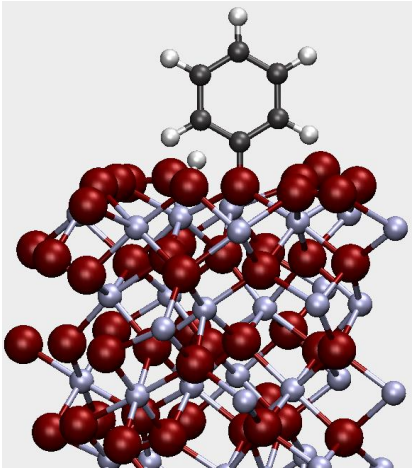
(111)





(100)





- The differential charge density shows a covalent bonding between the C (of benzene) and O (of In_2O_3) on (111) and (100) surface.

Conclusions

TECHNISCHE UNIVERSITÄT DARMSTADT

- Oxygen vacancies are shallow donor defects in In_2O_3 under reducing conditions
- Principal acceptor in In_2O_3 is the negative oxygen interstitial, whereas it is the tin vacancy in SnO_2
- Dopability of SnO_2 is exceeding that of In_2O_3 -> Proper dopands ?
- Oxygen self-diffusion is mediated by oxygen dumbbells and negative oxygen interstitials
- In_2O_3-(001) surfaces show a propensity towards electron depletion layers
- In polycrystalline ITO films large variations of the ionization potential can be expected
- (001) surfaces of ITO differ from those of pure In_2O_3
- Peroxide surfaces are destabilized by Sn doping; Oxide surfaces are stabilized by high Fermi energy and segregation of Sn
- STM contrast of ITO (001) surfaces can be explained qualitatively only by taking surface charging into account
- Adsorption of benzene favorable at In_2O_3-(100) and -(111) O-site
- Covalent bonding between C (of benzene) and O (of In_2O_3)