Aalto University
School of Chemical
Engineering

Surfaces and Films
CHEM E5150
Lecture 2A

J Koskinen

Items:

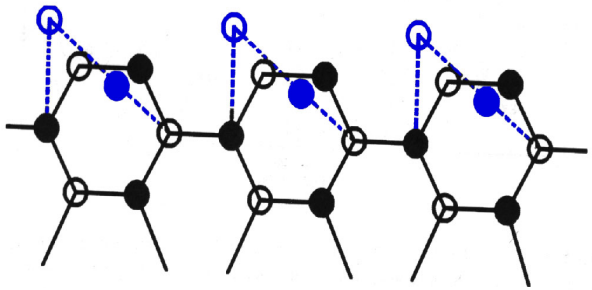
- **Ideal surfaces**
  - Surface energy
  - Surface structure
  - Restructuring
- **Real surfaces**
  - Contaminants
  - Functional groups
  - Deformation
- **Mechanical properties**
  - Roughness topography
  - Defects
- **Electronic properties**
  - DoS
- **Optical**

What is surface?
In ideal cases:

Surfaces are defined by ‘relaxed’ atoms (i.e. not constrained in 3D as their internal counterparts are). Dangling bonds from these surface atoms are free to react.

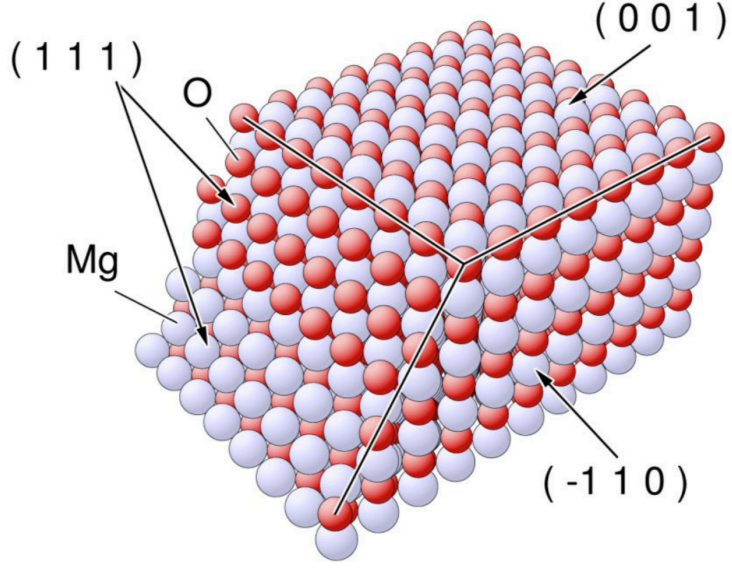
Relaxation of surface atoms leads to reconstruction (rearrangement of atoms near the surface).

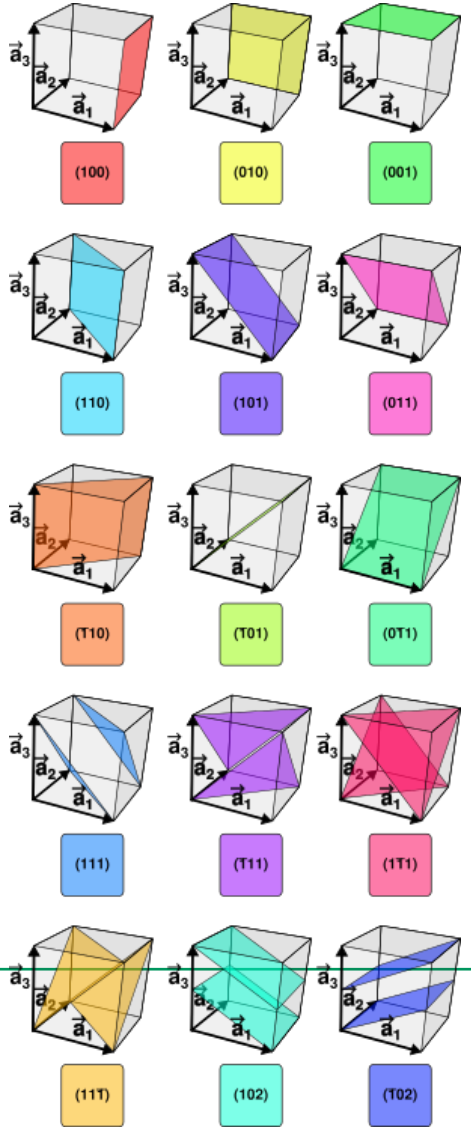
Relaxation and reconstruction are strongly influenced by the bonding type in the bulk material (i.e. metallic, covalent, ionic, and vander waals)



(110) Surface of GaAs. Surface atoms (blue) are ‘relaxed’ (i.e. not constrained in 3D).

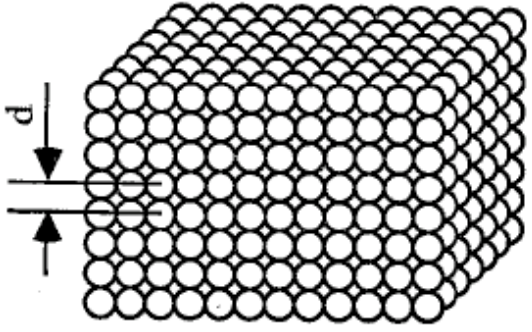
Miller Index



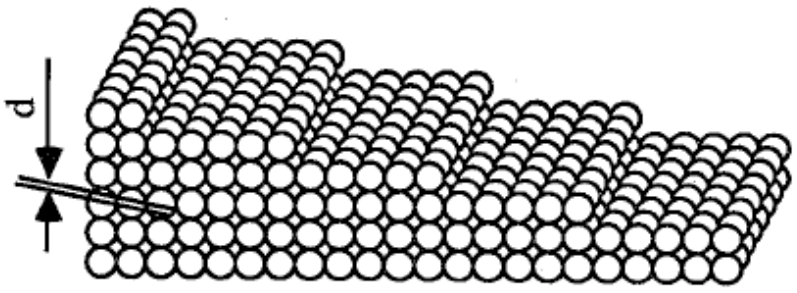


Wikipedia

Surface energy



Low-index surface



High-index surface consisting of low-index facets

$$\gamma(\mathbf{n}) = \frac{dW}{dA}$$

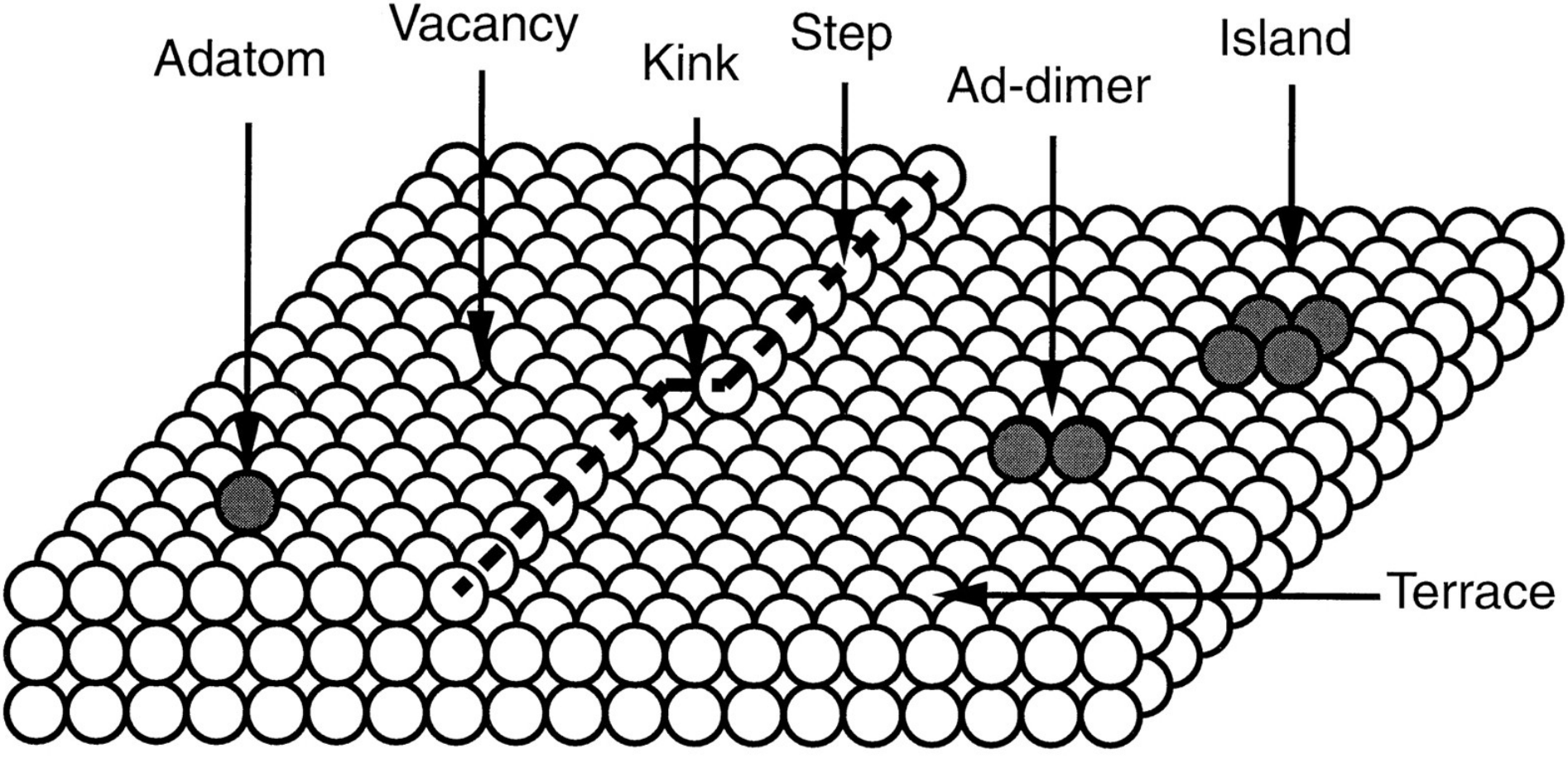
γ surface tension = *dW* work needed to form surface *dA*

In thermodynamic equilibrium:

$$\int_A dA\, \gamma(\mathbf{n}) = \min.$$

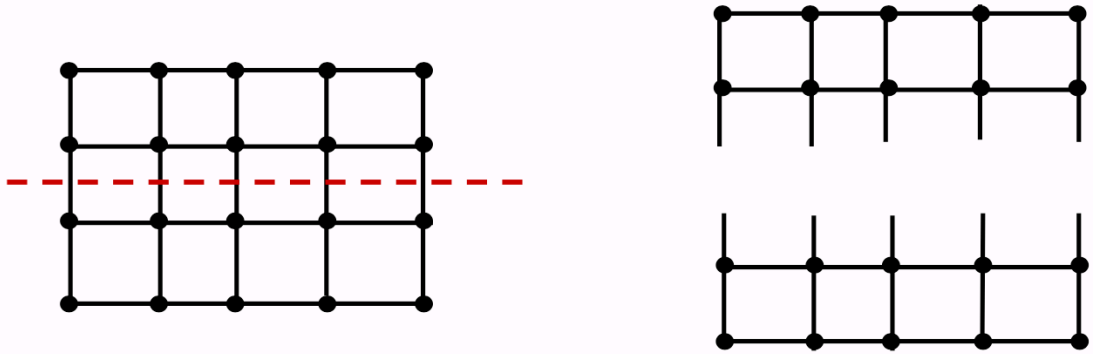
Surface atoms and defects

Science 18 Apr 1997:
Vol. 276, Issue 5311, pp. 377-383
DOI: 10.1126/science.276.5311.377



Solid and liquid Surfaces

In a nn pair potential model of a solid, the surface free energy can be thought of as the energy/ unit -area associated with bond breaking. :



work/ unit area to create new surface = $\frac{n}{A}\varepsilon \equiv 2\gamma$

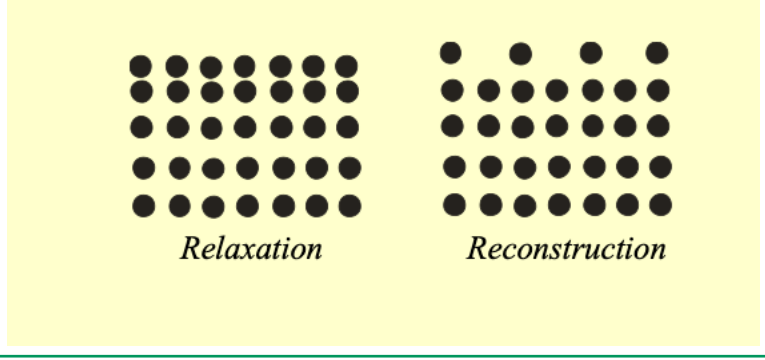
where *n/A* is the # of broken bonds / unit-area and the ε is the energy per bond i.e., the well depth in the pair-potential.

Then letting A = a² where a lattice spacing $\gamma \equiv \frac{\varepsilon}{2a^2}$

Relaxation and Reconstruction

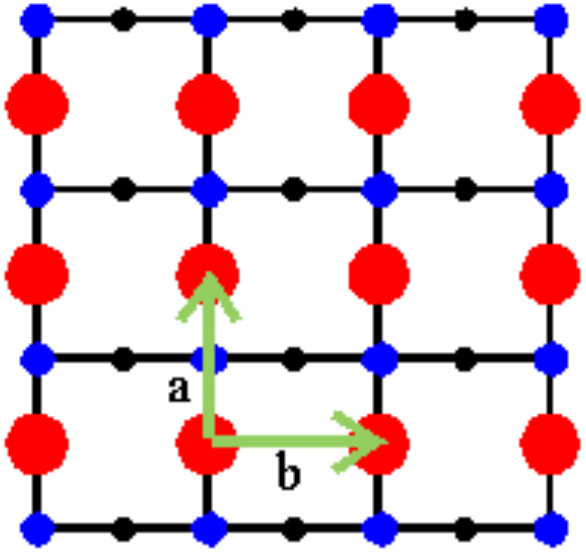
- Surfaces are not formed at zero temperature : Heat leads to atomic re-arrangement.

- Atoms at a surface have a lower co-ordination than those in the bulk – the origin of surface tension (strictly surface stress in a solid)

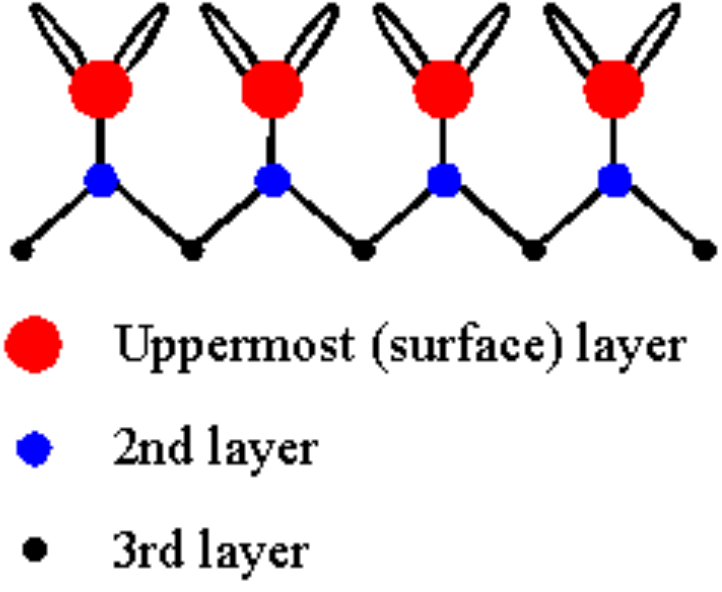


Example Si (100)

(a) UNRECONSTRUCTED Si(100)
(TOP VIEW)

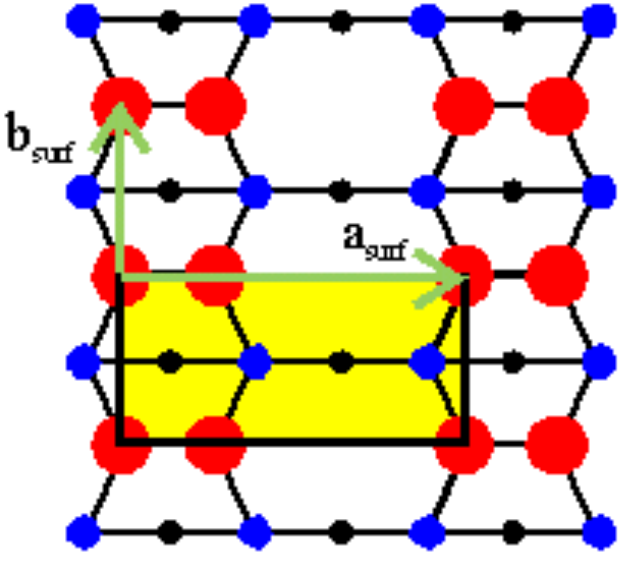


(b) UNRECONSTRUCTED Si(100)
(SIDE VIEW)

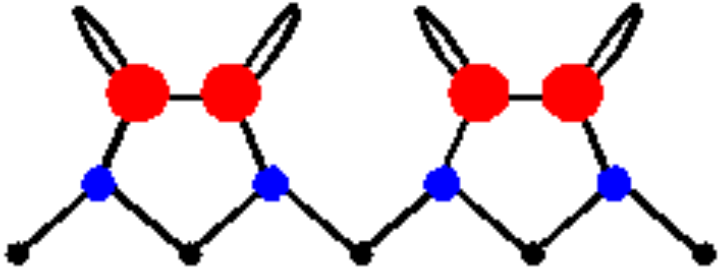


Example Si (100)

(a) RECONSTRUCTED Si(100)
(TOP VIEW)



(b) RECONSTRUCTED Si(100)
(SIDE VIEW)

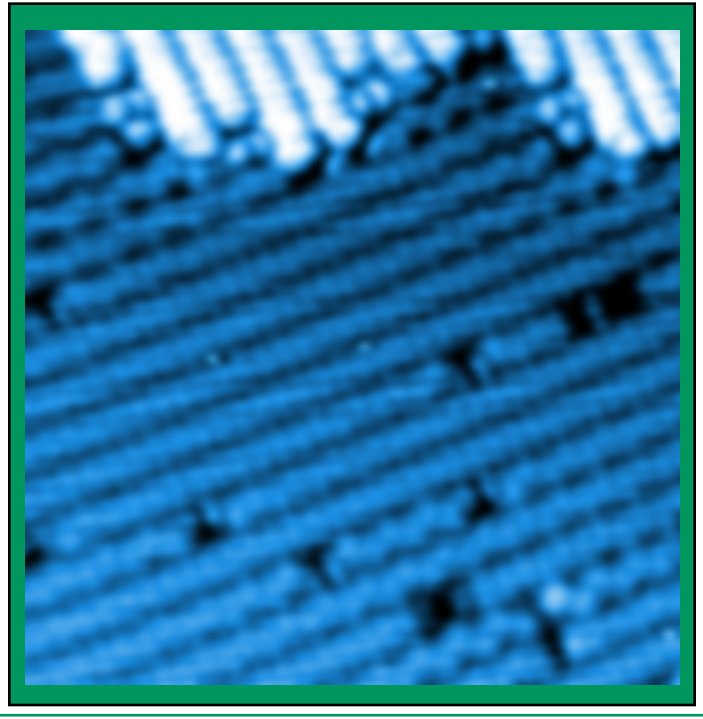


Uppermost (surface) layer

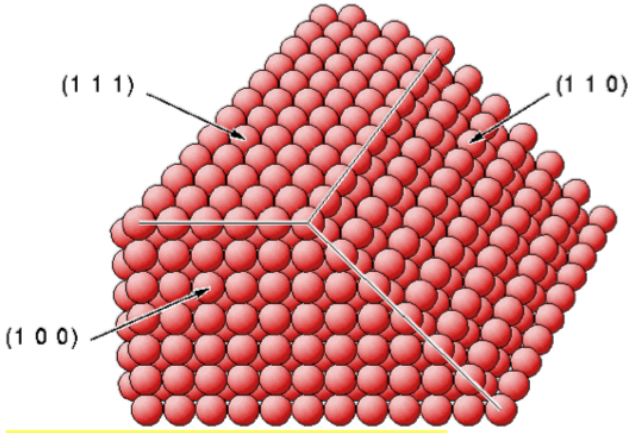
2nd layer

3rd layer

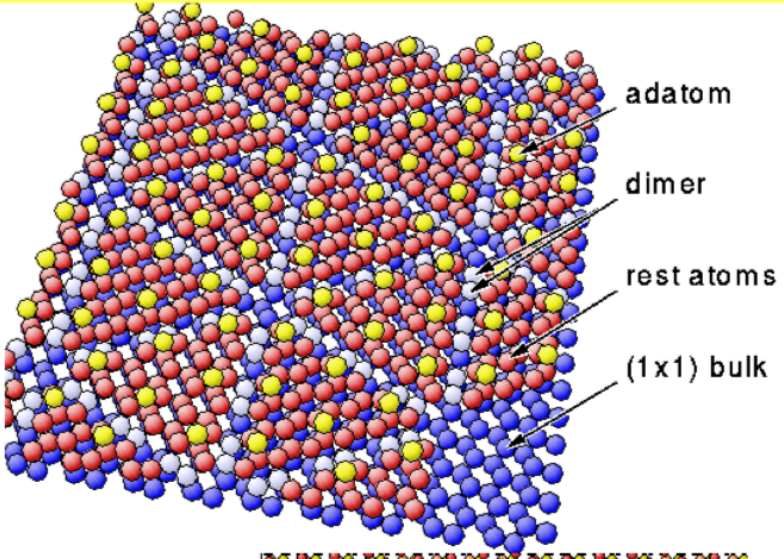
An STM image of the Si(100)-2x1 reconstruction



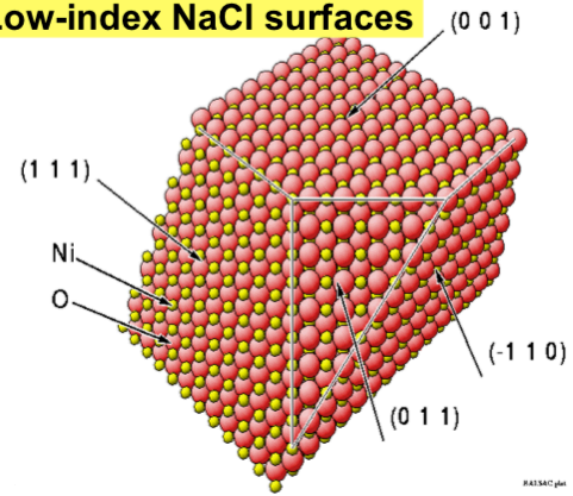
Low-index fcc metal surfaces



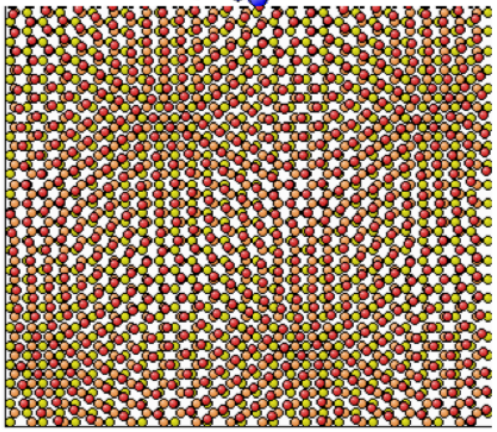
Si(111)-(7x7)—Dimer-adatom-stacking fault model



Low-index NaCl surfaces



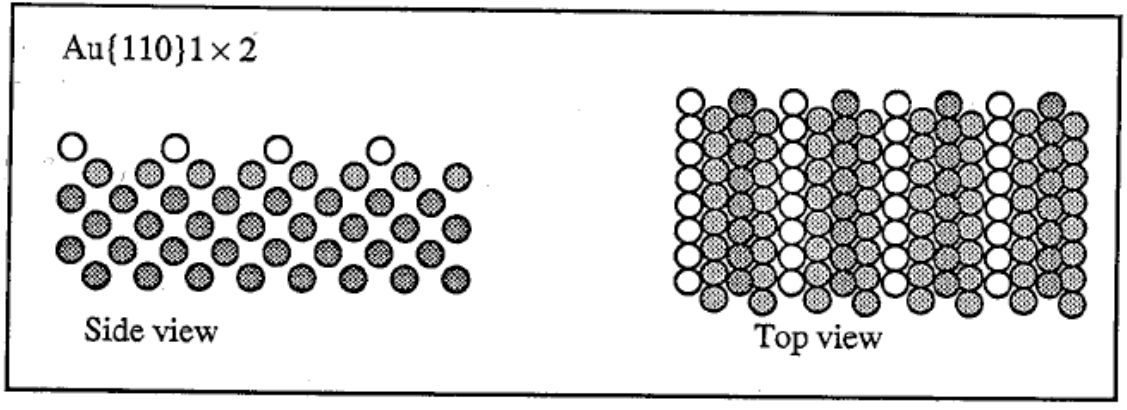
Fcc(111) super-lattice = a Moiré pattern: 4 degree rot'n.

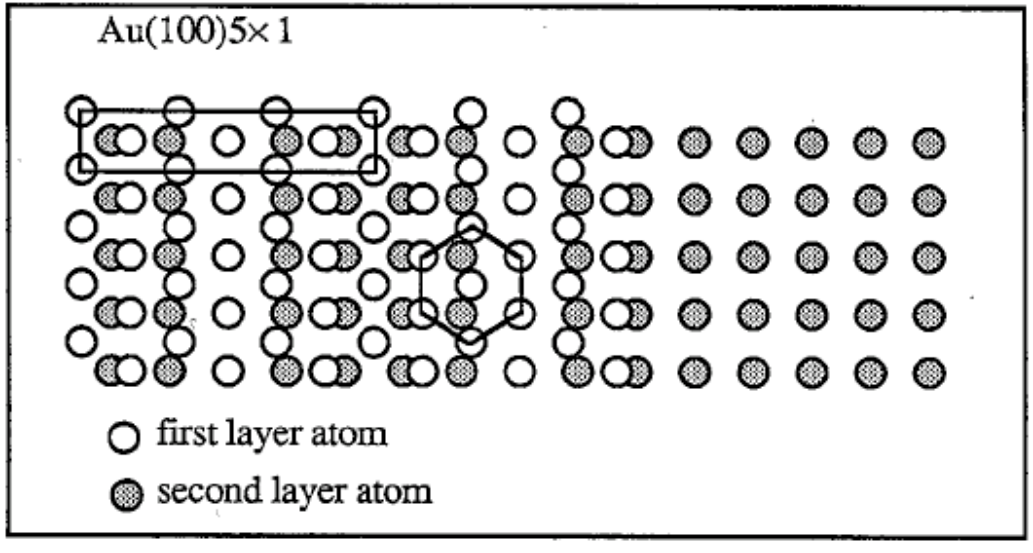


http://www.fhi-berlin.mpg.de/th/personal/hermann/pictures.html

A

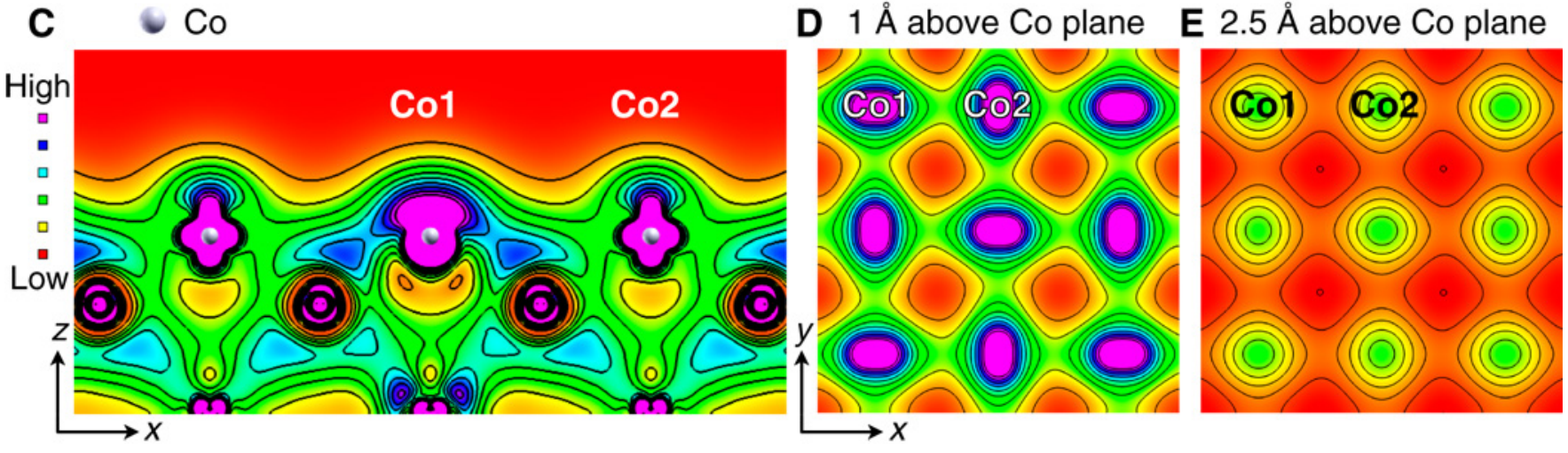
Au surface reconstruction





Modelling of surface electron density

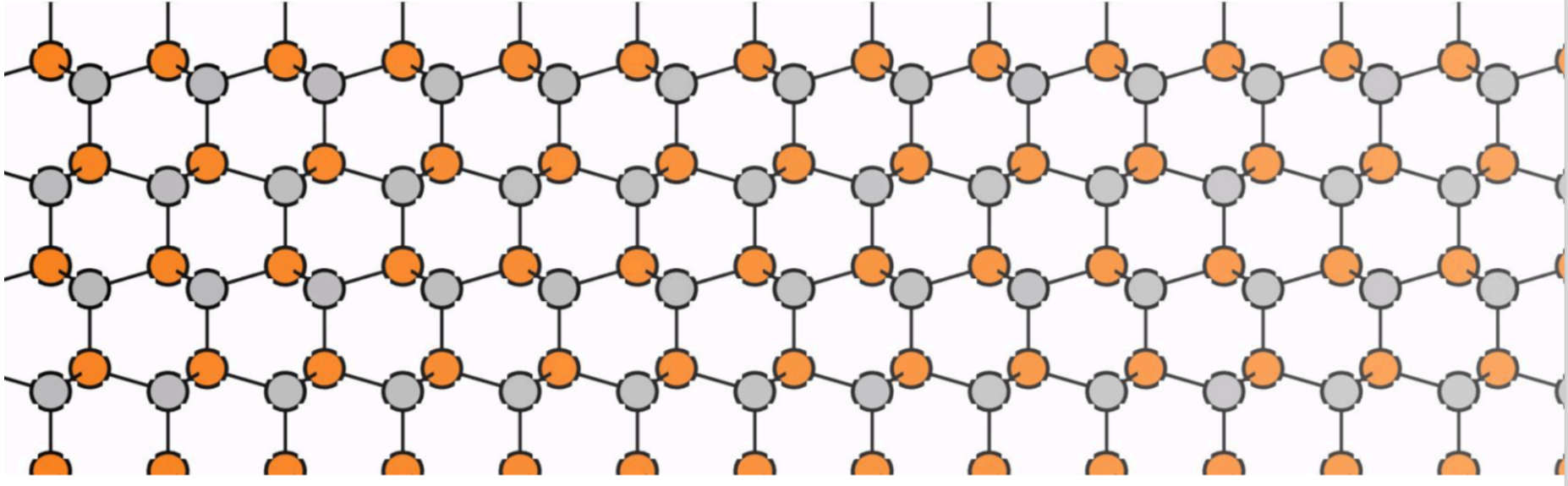
Surface electron density on $CeCoIn_5$.



Science Advances 22 Sep 2017:
Vol. 3, no. 9, eaao0362
DOI: 10.1126/sciadv.aao0362

Surface energy

Energy is proportional to the number of bonds broken.



Surface energy - milled index

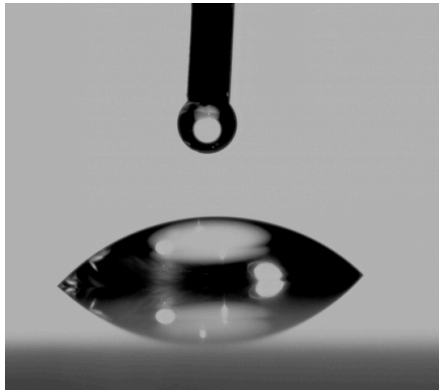
$$\gamma_{\{100\}} = \frac{4\varepsilon}{a^2} = 4.0 \frac{\varepsilon}{a^2}$$

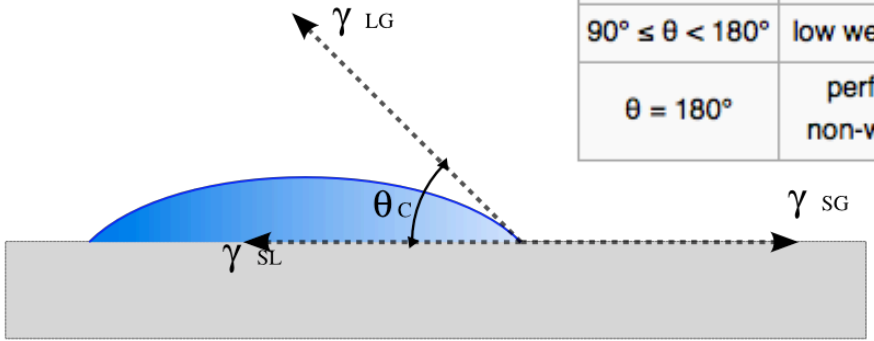
$$\gamma_{\{110\}} = \frac{5}{2^{0.5}} \frac{\varepsilon}{a^2} = 3.54 \frac{\varepsilon}{a^2}$$

$$\gamma_{\{111\}} = 2(3)^{0.5} \frac{\varepsilon}{a^2} = 3.46 \frac{\varepsilon}{a^2}$$

Contact angle

Contact angle	Degree of wetting
θ = 0	Perfect wetting
0 < θ < 90°	high wettability
90° ≤ θ < 180°	low wettability
θ = 180°	perfectly non-wetting





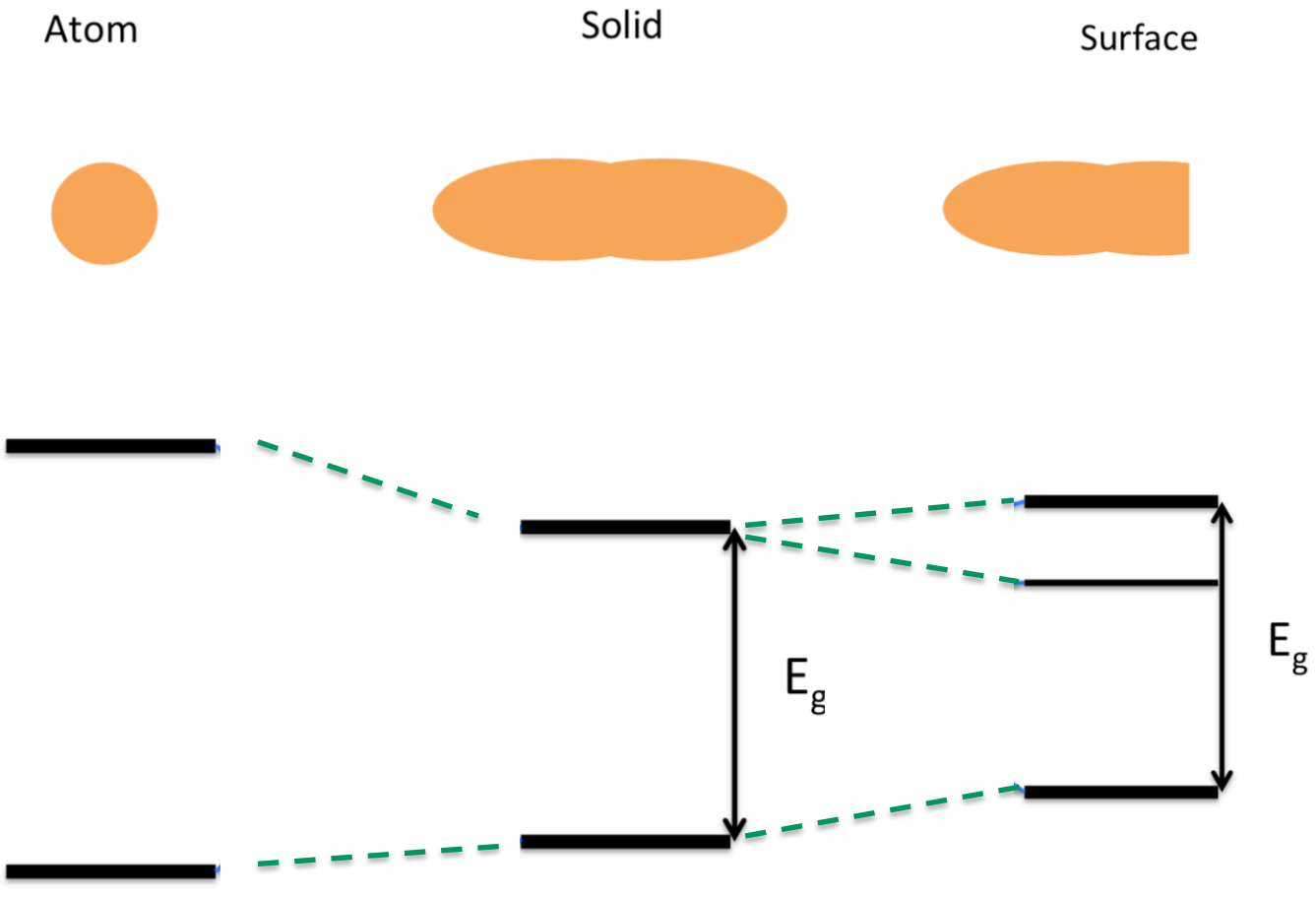
$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta$$

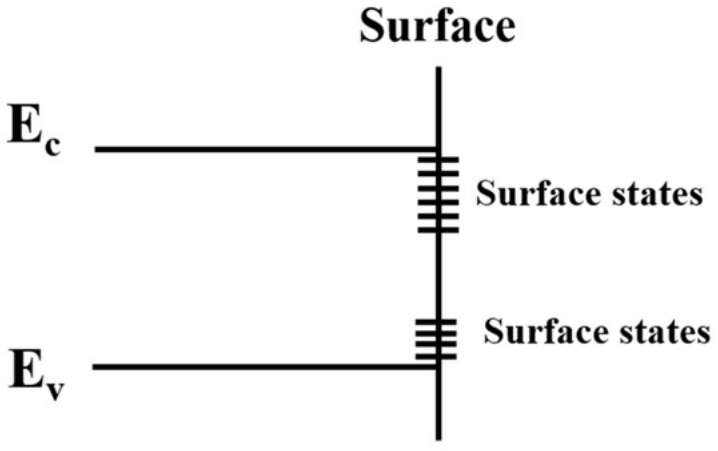
$$S = \gamma_{LG}(\cos\theta - 1)$$

Young equation
S solid
L liquid
G gas

Spreading parameter *S*
Complete wetting when $S \approx 0$
non-wetting when $S \approx -2\,\gamma_{LG}$

Surface Electronic States

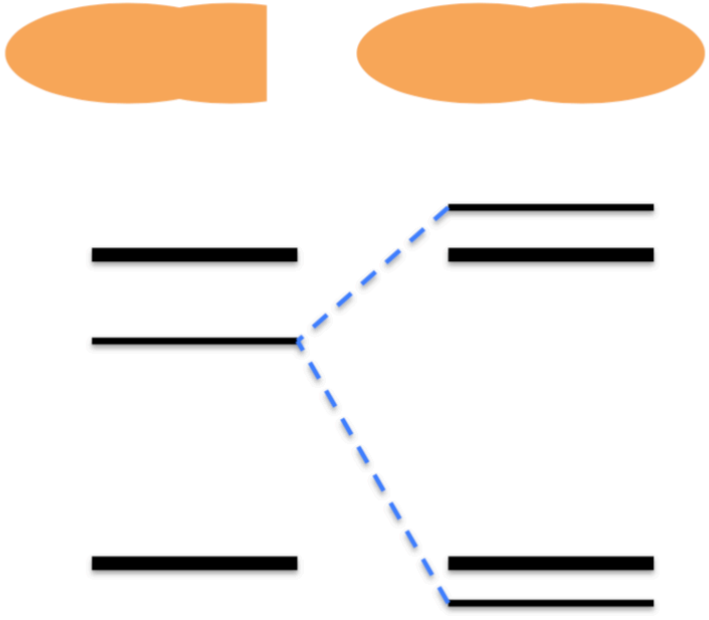


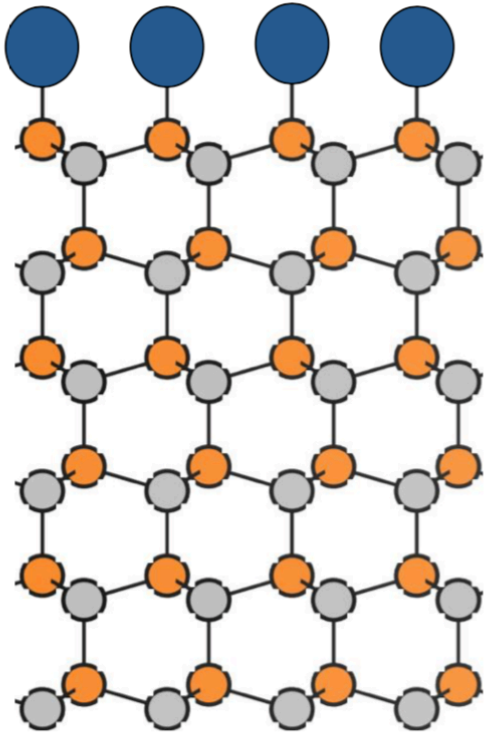


10.3390/nano10020362

Surface passivation

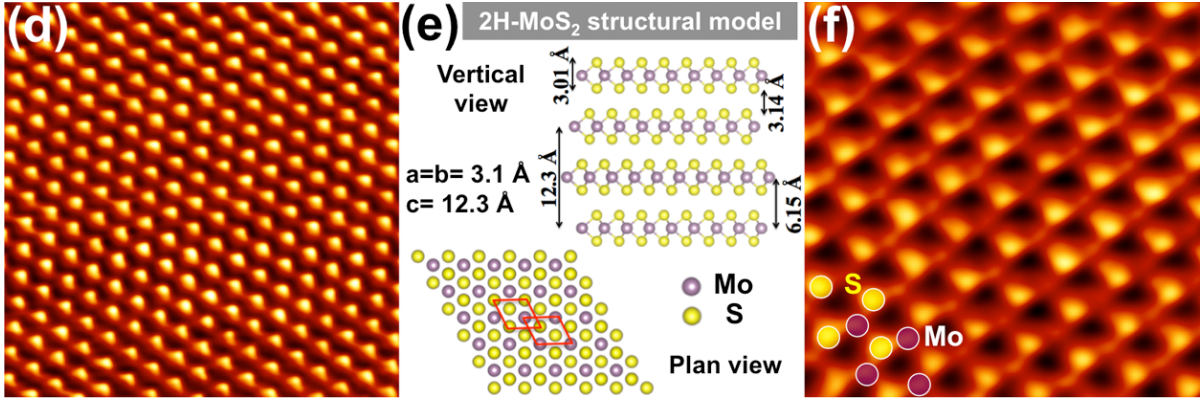
- Chemical passivation





Dr. Keith T. Butler Department of Chemistry k.t.butler@bath.ac.uk

Clean surface (0001) of MoS_2

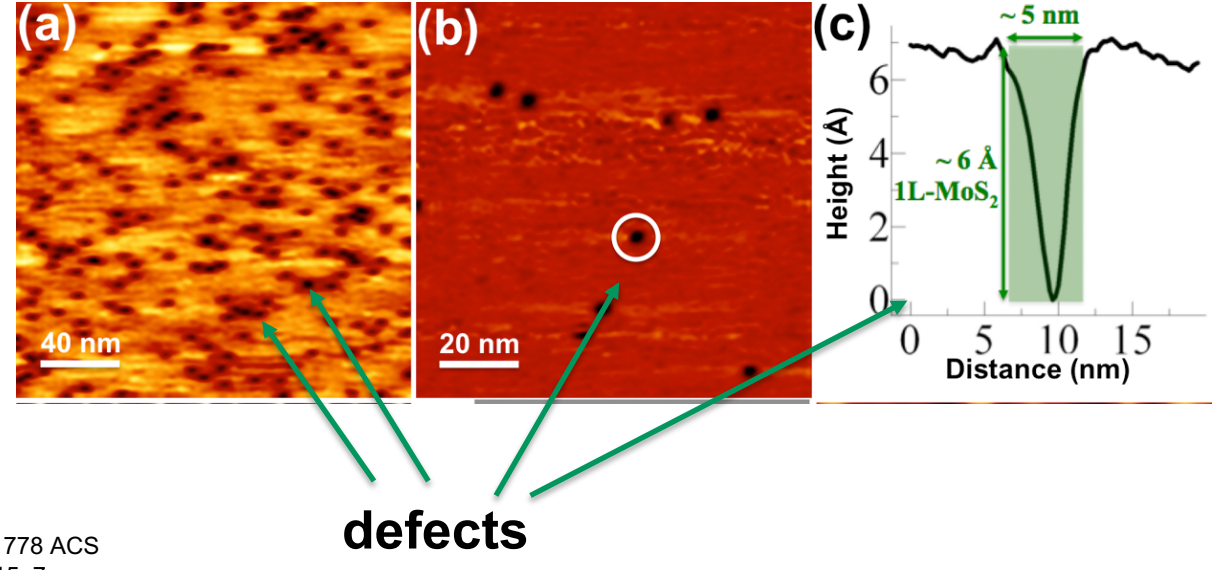


DOI: 10.1021/acsami.5b01778 ACS Appl. Mater. Interfaces 2015, 7, 11921−11929

Aalto University
School of Chemical Engineering

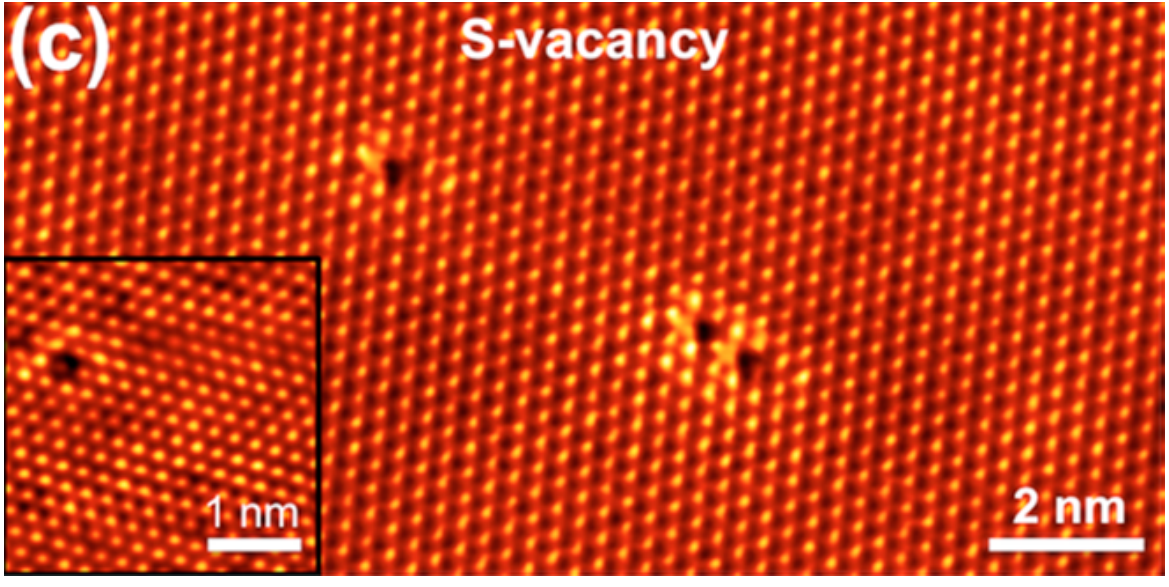
Figure 1. Topography of the "as-exfoliated" MoS_2 crystal from both sources. (a) Large STM image (V_{bias} = +1.5 V, I_t = 0.3 nA) exhibits dark defects with high defect density. (b) STM image (V_{bias} = −300 mV, I_t = 0.5 nA) recorded on low defect density area. (c) Line profile taken across the dark defect outlined in panel b; the green box shows an example of the defect dimensions (5 nm × 0.6 nm). (d) High resolution STM image (5 nm × 5 nm, V_{bias} = +150 mV, I_t = 0.2 nA, R_{gap} = 750 MΩ) shows a hexagonal pattern in defect-free area. (e) Schematic representation of the 2H-MoS_2 bulk structure. The 2H-MX_2 polytype possess trigonal prismatic coordination that has two X−M−X layers per unit cell. (f) Well-resolved STM image (2.5 nm × 2.5 nm, V_{bias}=+100 mV, I_t = 2.3 nA, R_{gap}= 43.5 MΩ) showing both S- and Mo-layer structure presented by the bright and moderate contrast, respectively.

Clean surface (0001) of MoS_2 with defects



DOI: 10.1021/acsami.5b01778 ACS Appl. Mater. Interfaces 2015, 7, 11921−11929

Clean surface (0001) of MoS_2 with defects



Clean surface (0001) of MoS_2 with its impurities

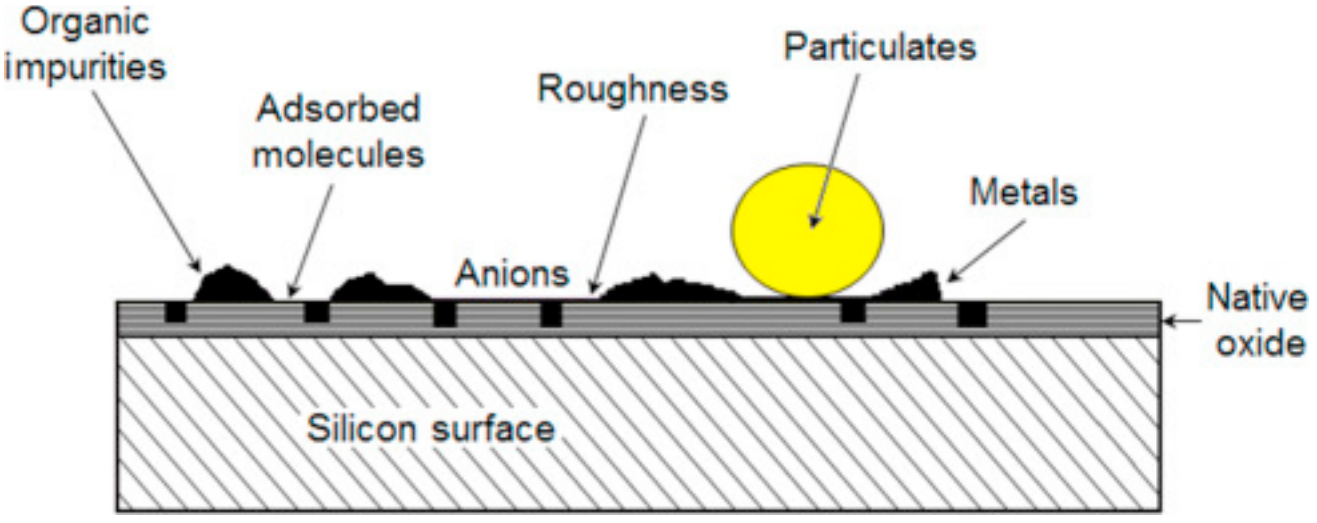
Table 1. Comparison of ICPMS Data Collected on Both MoS_2 Sources[a]

	abundance (ppb)										
	Al	Ca	Cu	Fe	Mg	Mn	P	Na	Ti	W	Zn
a-MoS_2	52.6	5.7	21.3	44.3	2.32	2.31	10.5	18.7	1.4	6.68	7.8
c-MoS_2	9.6	<1.0	<1.0	37.4	<1.0	<1.0	5.0	2.82	2.17	1.84	<1.0

[a]The abundance unit is parts-by-billion by weight.

Inductively Coupled Plasma Mass Spectrometer

Surface contamination



5 major contaminant classes (in CMOS processes)

- Particles
- Metallic ions
- Chemicals
- Bacteria
- Airborne molecular contaminats

Optical properties of real thin films

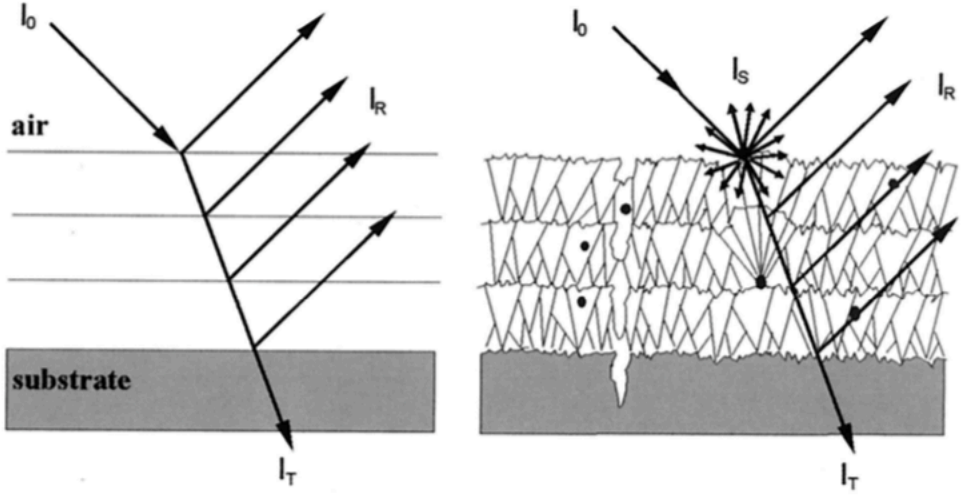


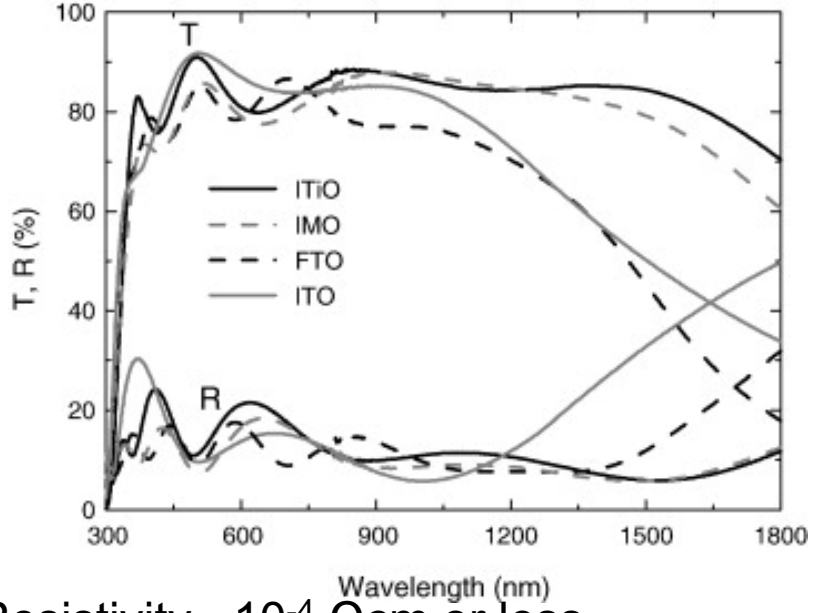
Fig. 1. Left, ideal single-crystalline substrate coated with ideal single-crystalline films. Incoming light with intensity I_0 is split into reflected and transmitted parts I_R and I_T, respectively. Conservation of energy is given by $I_0 = I_R + I_T$. Right, real substrate with real coatings. Part of incoming intensity I_0 is absorbed (I_A) or scattered (I_S). Conservation of energy is given by $I_0 = I_R + I_T + I_A + I_S$.

1 June 2002 / Vol. 41, No. 16 / APPLIED OPTICS

Transparent – semi transparent

- Photovoltage
- Controlled emission
- Decoration

TCO (transparent conductive oxides) films



ITO Indium Sn oxide
IMO Indium Mo oxide
ITiO Indium Ti oxide
FTO Tin oxide + fluorine

Resistivity ~10^{-4} Ωcm or less

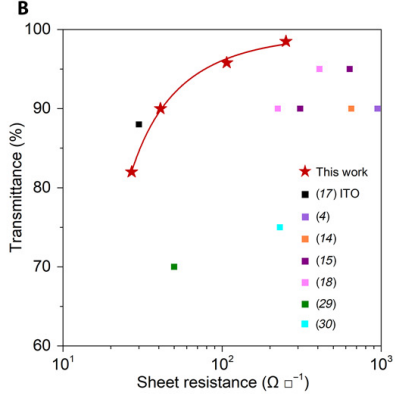
Table 1. TCO Compounds and dopants.

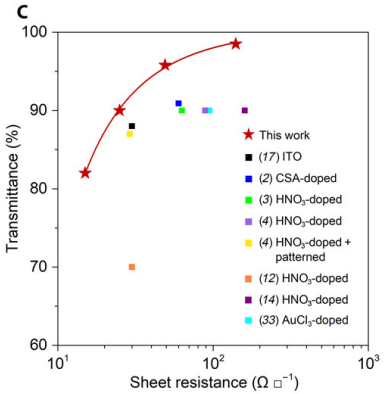
TCO	Dopant
SnO_2	Sb, F, As, Nb, Ta
ZnO	Al, Ga, B, In, Y, Sc, F, V, Si, Ge, Ti, Zr, Hf, Mg, As, H
In_2O_3	Sn, Mo, Ta, W, Zr, F, Ge, Nb, Hf, Mg
CdO	In, Sn
$GaInO_3$	Sn, Ge
$CdSb_2O_3$	Y

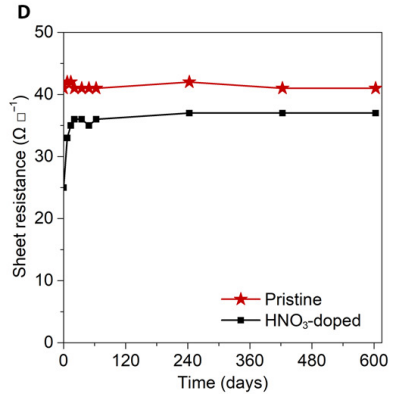
Charge carries due to oxygen vacancies and dopand impurities

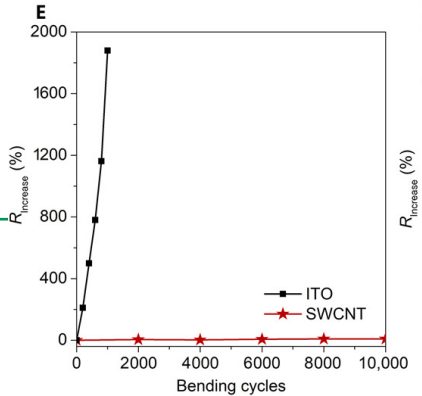
https://doi.org/10.1016/j.tsf.2009.09.044
https://doi.org/10.1515/rams-2018-0006

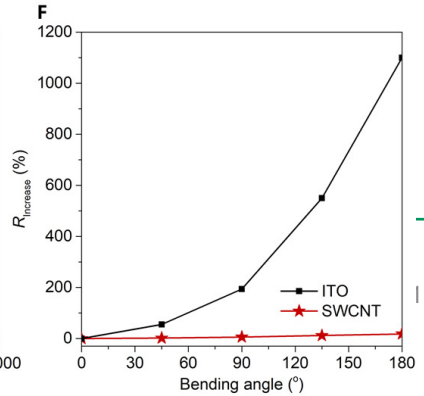
Transparent conductive layer





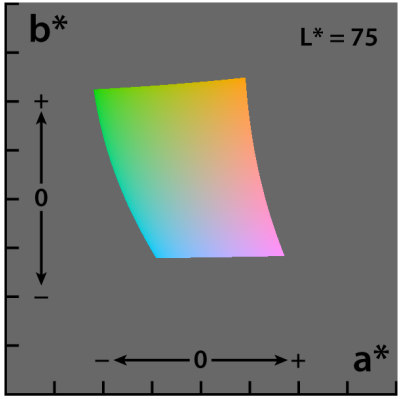


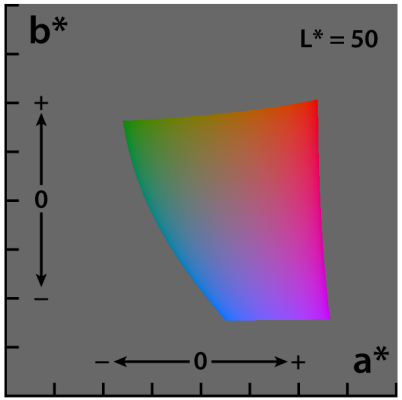


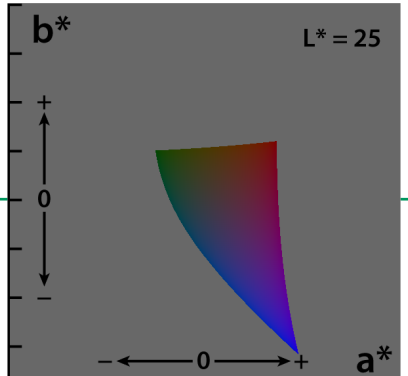


Color map
L* a* b*

The **CIELAB color space** (International Commission on Illumination - CIE in 1976)







Arc deposited Ti-Mg-N
Effect of composition

Table 6 *L* a* b** color coordinates, and conductivity of (Ti,Mg)N coating as a function of Mg/Ti composition[a]

I_{Mg} (A)	Mg/Ti Atomic ratio	A (nm)	Color coordinate values			ρ (μΩcm)
			L*	a*	b*	
0	0	0.4306	78.6	1.0	35.2	98
0.1	0.03	0.4294	78.4	0.0	23.3	106
0.3	0.09	0.4301	75.0	2.6	26.3	110
0.2	0.22	0.4314	65.5	11.8	25.9	175
0.6	0.24	0.4320	64.7	12.3	25.5	183
0.5	0.41	0.4327	55.7	11.3	3.9	338
0.7	0.48	0.4331	55.4	7.5	0.4	406
0.7	0.53	0.4337	56.7	1.8	−1.5	457

[a] *Martin, P.; Bendavid, A. Review of the Filtered Vacuum Arc Process and Materials Deposition.* Thin Solid Films ***2001***, 394 *(1), 1–14.*

Mg/Ti ratio 0 → 0.53
- colors golden → copper → violet → metallic gray
- conductivity 98 → 457 *μΩcm*

Bulk Plasmons

Free electron gas with an applied oscillatory electric field

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}_0 e^{i\omega t}$$

Equation of motion

$$m\ddot{x}=-e\mathbf{E}_0 e^{i\omega t}$$

Solution: $x=x_0 e^{i\omega t}$

$$x_0=\frac{eE_0}{m\omega^2}$$

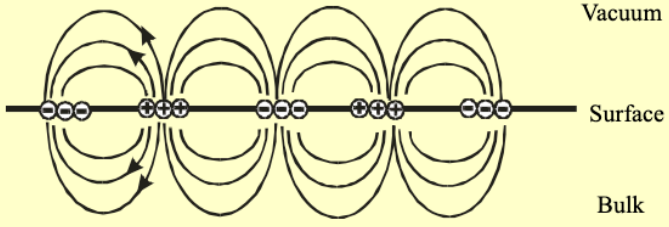
$$\omega_p^2=\frac{ne^2}{\varepsilon_0 m} \qquad \omega_p \sim 10^{15}\text{Hz}$$

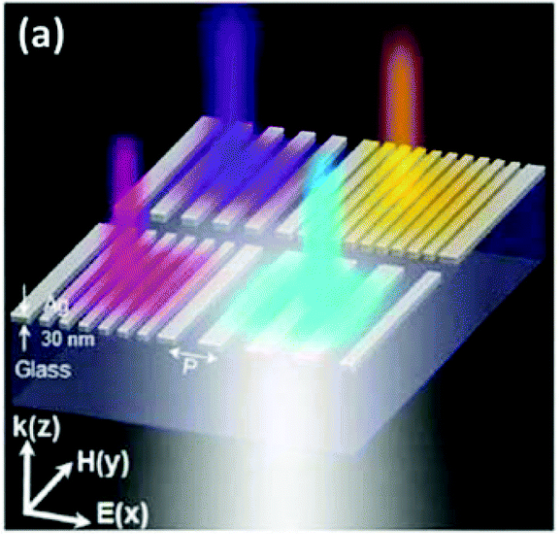
For a longitudinal electromagnetic wave to exist $\varepsilon_r(0,\omega)=0 \longrightarrow \omega=\omega_p$

Introduction to Surface Physic, N. Tabet

Surface plasmos

Surface Plasmons: Charge oscillations at a surface





https://doi.org/10.1039/C5NR00578G

$$\omega_{sp} = \frac{\omega_p}{\sqrt{2}}$$

Introduction to Surface Physic, N. Tabet