Fabrication of nanostructures and nanoscale devices.
Part 3.

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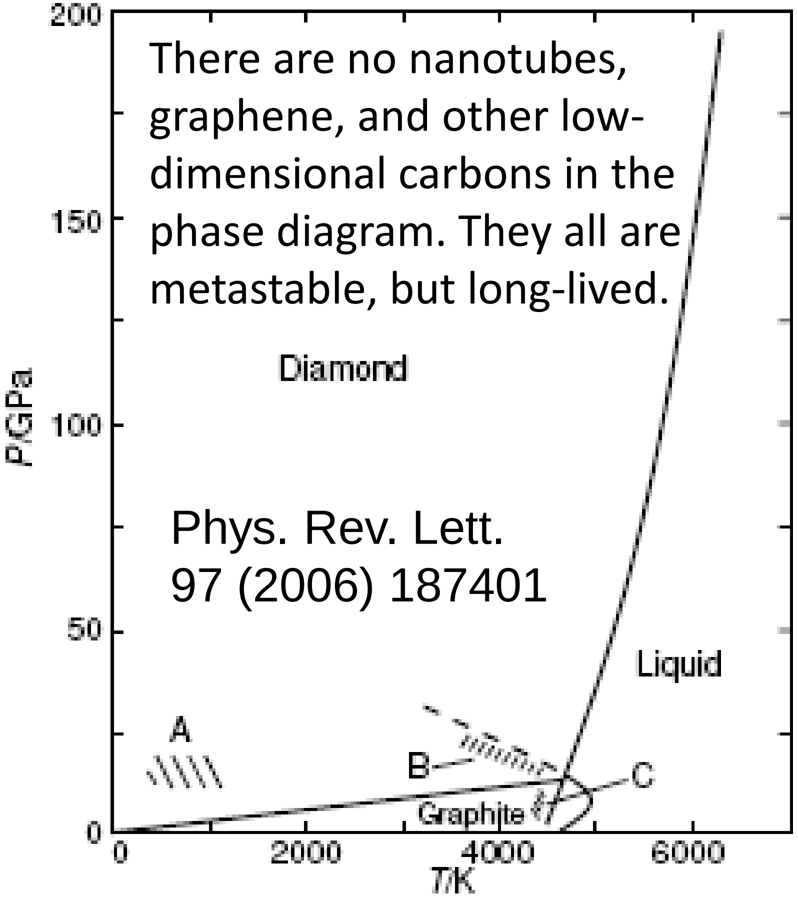
See the lectures at https://www.nanocenter.si/qt-future/education-2/

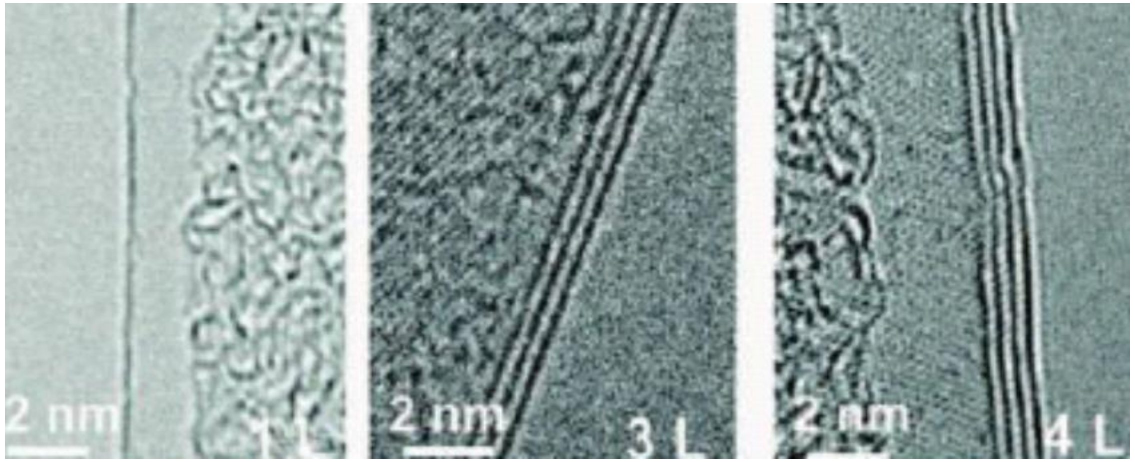
<reformulated> What is the difference of graphite and graphene?

Q2

There are no nanotubes, graphene, and other low-dimensional carbons in the phase diagram. They all are metastable, but long-lived.

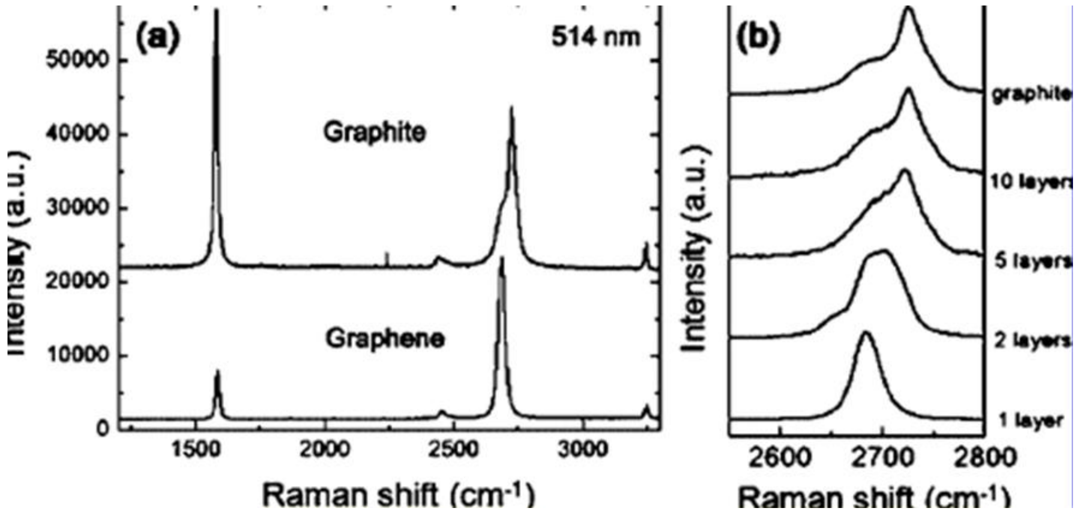


Phys. Rev. Lett. 97 (2006) 187401



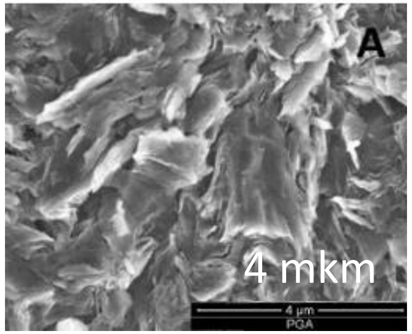
TEM images

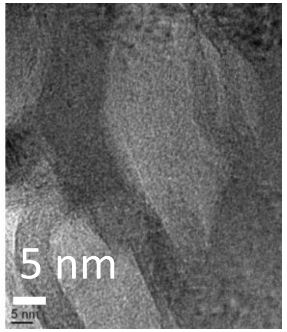
Nano Letters 9 (2009) 30



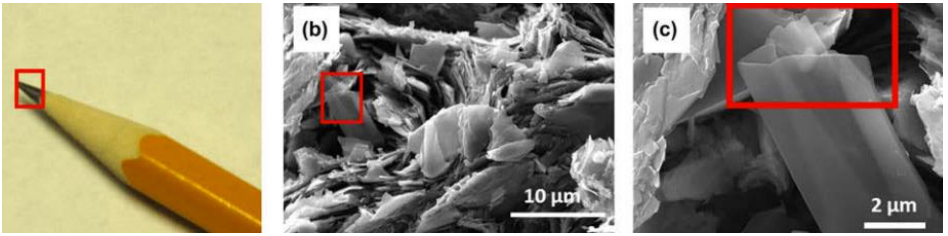
How to recognize the number of layers?

Phys. Rev. Lett. 97 (2006) 187401





Nuclear graphite = heat-treated coke, J. Phys.: Conf. Ser. 371 (2012) 012017



Pencil lead: graphite + clay, J. Mater. Res. 31 (2016) 2578

Parts 3-4, Outline

Fabrication of Thin Films (2D fragments of nanostructures)

• Atomically flat supports (etching, polishing, termination)

• Exfoliation of ‘van der Waals’ thin films

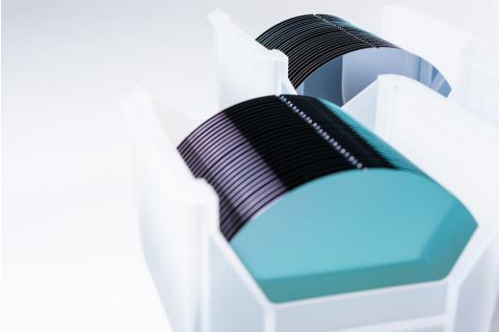
• Chemical vapor deposition (CVD) (graphene; what else can be deposited)

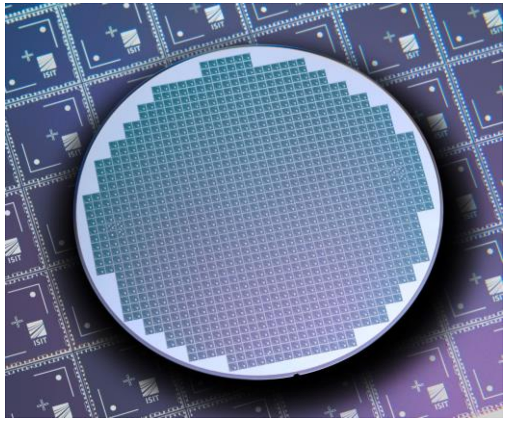
• Epitaxial films (molecular beam epitaxy (MBE), atomic layer deposition (ALD))

Will be continued on Nov 3 (Pt 4):

•Physical vapor deposition (thermal, laser, magnetron; growth control and monitoring)
•Wet deposition (electroless)
•Wet deposition (electrochemical)

Silicon supports (wafers)





Chemical etching: oxide formation and dissolution

HNO_3 + HF ($+CH_3COOH + H_2O$)

nitric acid (oxidizer) — hydrofluoric acid (F^- forms soluble species) — acetic acid (improves wetting)

$HNO_2 + HNO_3 = 2NO_2 + H_2O$

nitrous acid (impurity in nitric acid)

$Si \rightarrow SiO_2$ → **$SiO_2 + 6HF = H_2SiF_6 + H_2O$**

the rate depends on the temperature

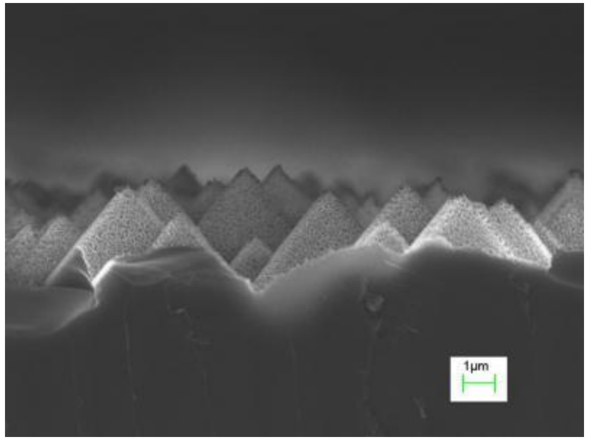
the rate depends on HF concentration

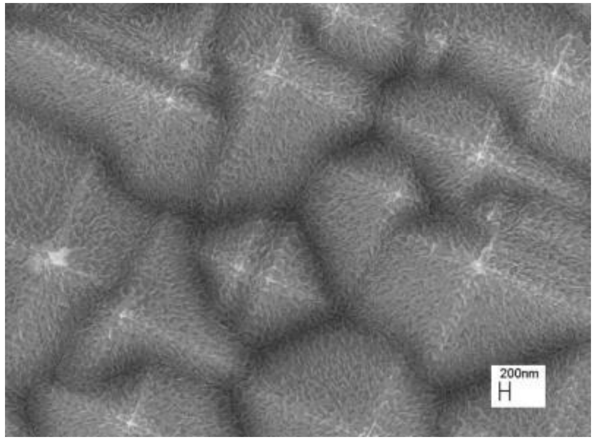
There are hundreds of recipes and commercial etchants. Dry (gas plasma) etching is also possible, known as Reactive ion etching (RIE).

Dopants:
B, P, N, metals

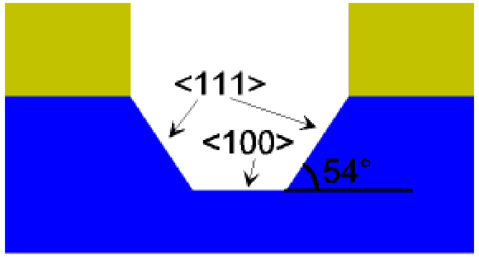
Orientations:
(100) is the most Usual

Oxide: 10 – 300 nm



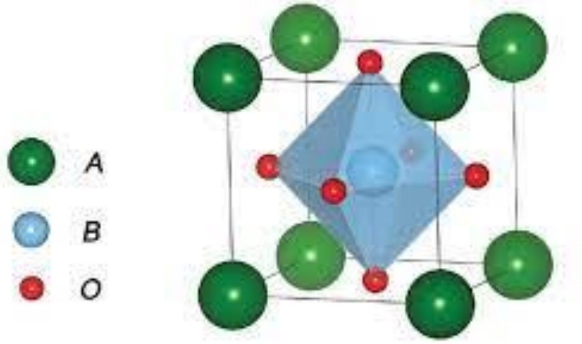


«Pyramidal» etching in H_2O_2+HF

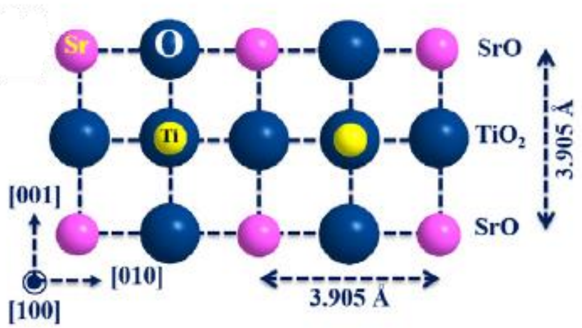


Perovskite supports (ABO_3)

Substrate	Orientation	Structure	Lattice constants (Å)
$NdScO_3$	(1 1 0)	Orthorhombic	$a = 5.57$ $b = 5.77$ $c = 7.99$
$KTaO_3$	(0 0 1)	Cubic	$a = 3.988$
$GdScO_3$	(1 1 0)	Orthorhombic	$a = 5.48$ $b = 5.76$ $c = 7.92$
$DyScO_3$	(1 1 0)	Orthorhombic	$a = 5.54$ $b = 5.71$ $c = 7.89$
$SrTiO_3$	(0 0 1), (1 1 0), (1 1 1)	Cubic	$a = 3.905$
$La_{0.18}Sr_{0.82}Al_{0.59}Ta_{0.41}O_3$ (LSAT)	(0 0 1)	Cubic	$a = 3.88$
$NdGaO_3$	(0 0 1), (1 1 0)	Orthorhombic	$a = 5.43$ $b = 5.50$ $c = 7.71$
$LaAlO_3$	(0 0 1)	Rhombohedral	$a = 3.78$
$SrLaAlO_4$	(0 0 1), (1 0 0)	Tetragonal	$a = 3.75$ $c = 12.63$
$YAlO_3$	(1 1 0)	Orthorhombic	$a = 5.18$ $b = 5.33$ $c = 7.37$



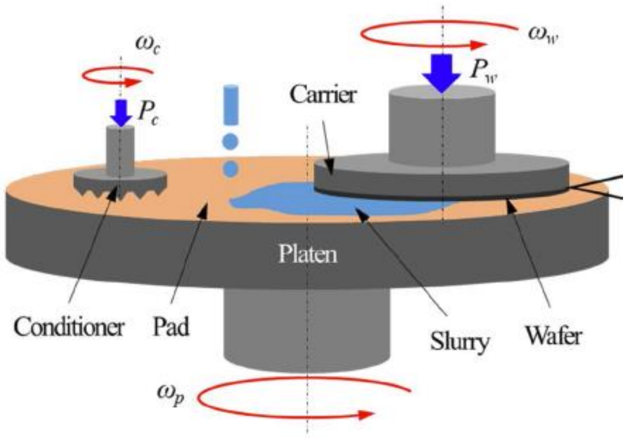
$SrTiO_3$(001), Ti-terminated



Progr. Surface Sci. 92 (2017) 117

General scheme of support pretreatment

Cutting and polishing first



Clean (Acetone/methanol): Removes dust particles, contaminants from the top surface

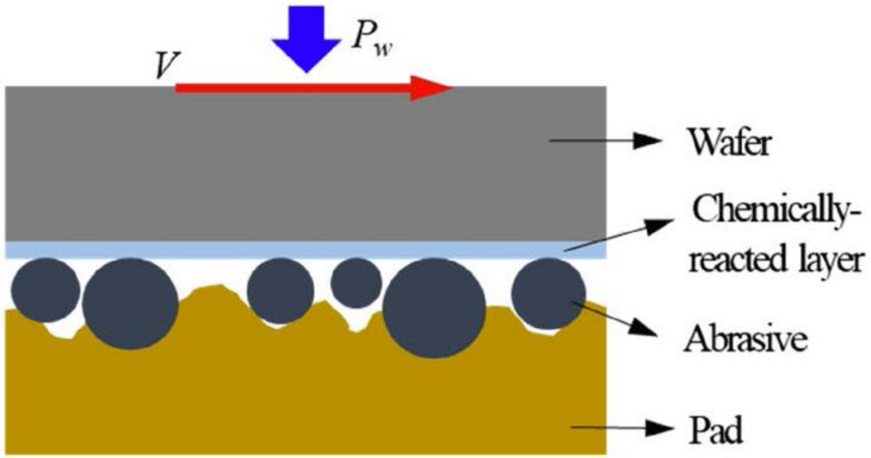
→ **Soak (Deionized water)**: AO_x or BO_y of ABO_3 surface reacts with water to form hydroxide complexes

→ **Etch (Acidic solution)**: Hydroxide complexes dissolves in the acidic solution

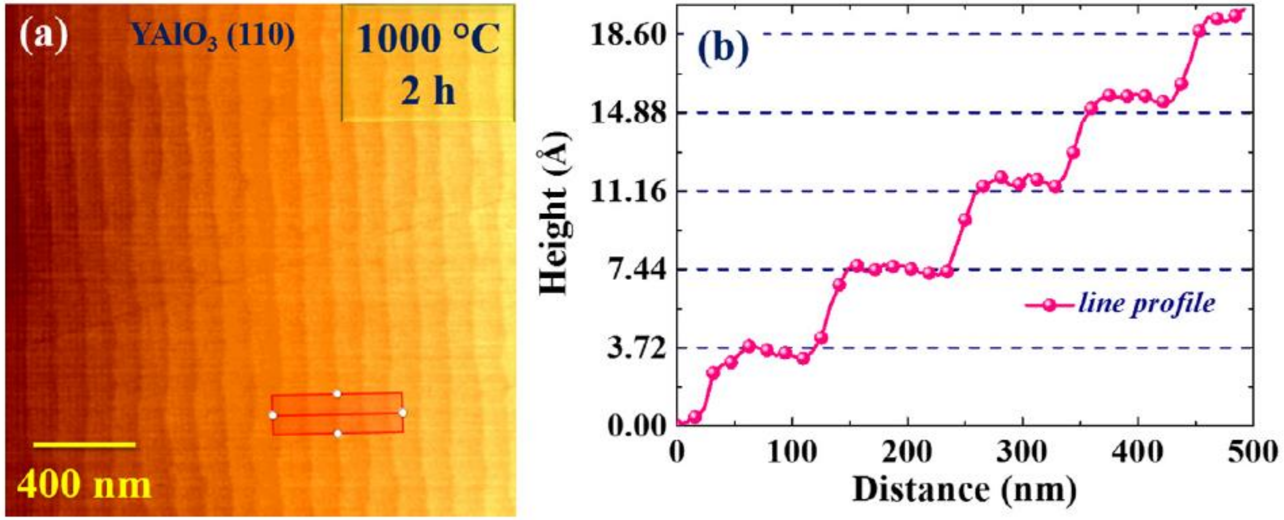
→ **Soak (Deionized water)**: Dissolves extra components formed due to wet acidic etching

→ **Dry (Nitrogen gas)**: Removes extra components to prevent any further reaction

→ **Anneal (T ~ 1000° C)**: Surface reconstruction to produce atomically flat surface

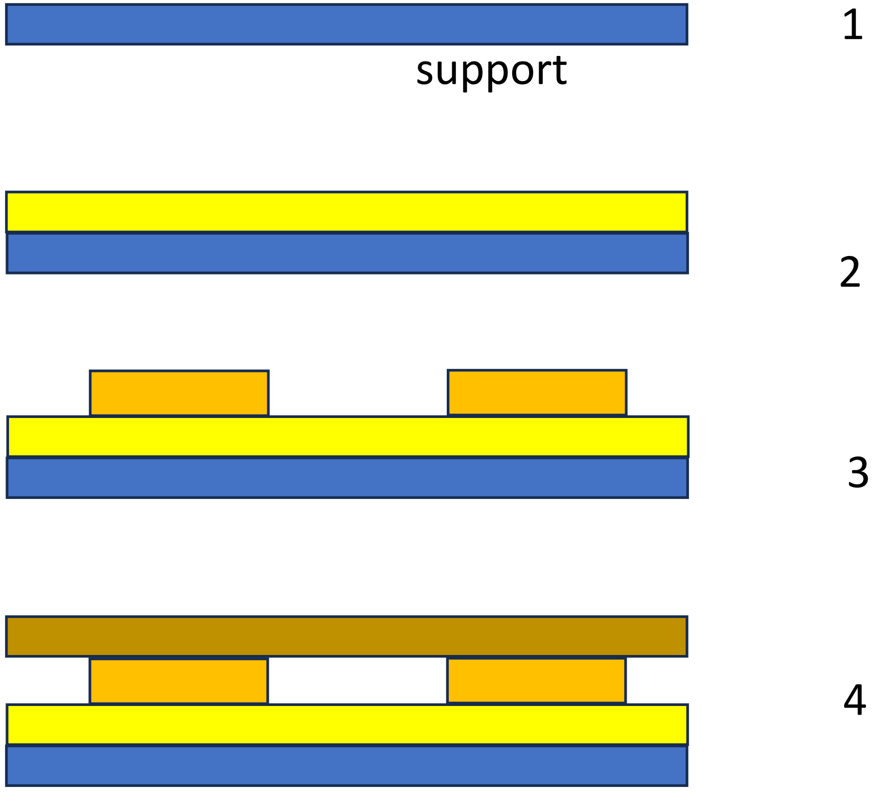


Int. J. Precision Eng. Manufact. 9 (2022) 349

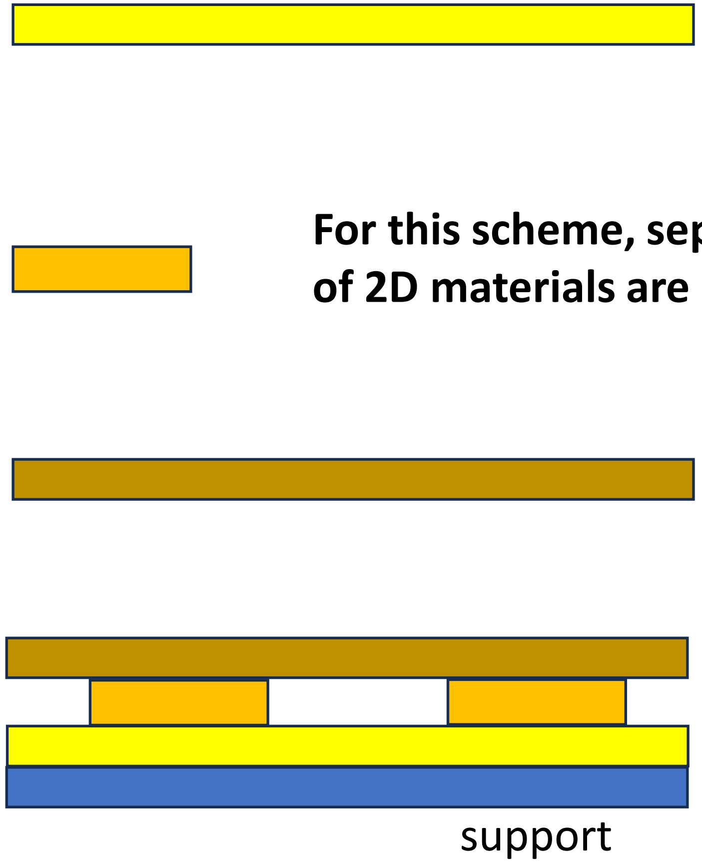


To construct some nanostructure on support, we can follow two different technological schemes

Subsequent deposition



Fabrication of fragments and their immobilization

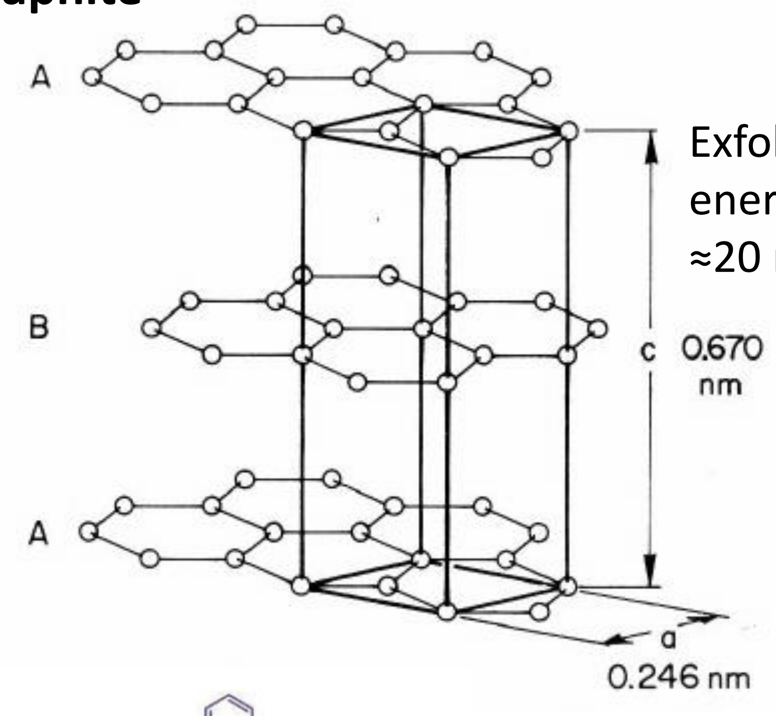


For this scheme, separate flakes of 2D materials are required

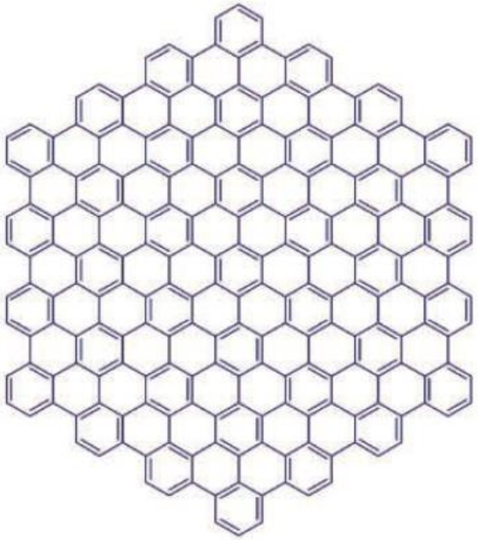
‘Mixed’ schemes are also possible

Graphite

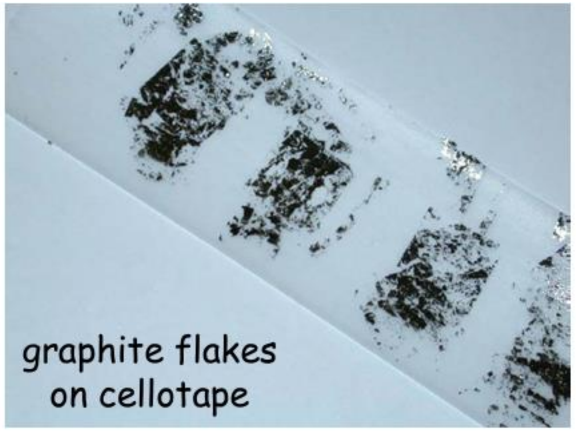
Layered crystal structures, which allow exfoliation

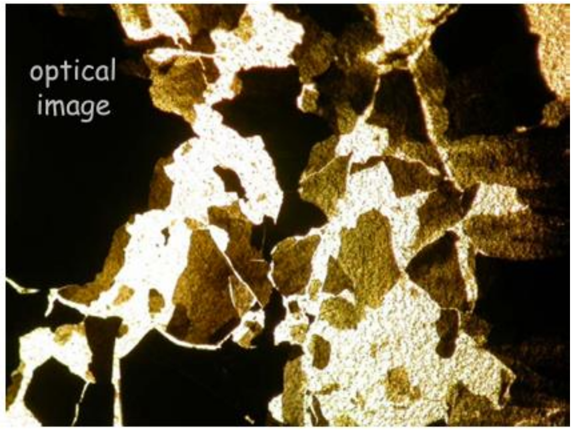


Exfoliation energy ≈20 meV Å^{-2}

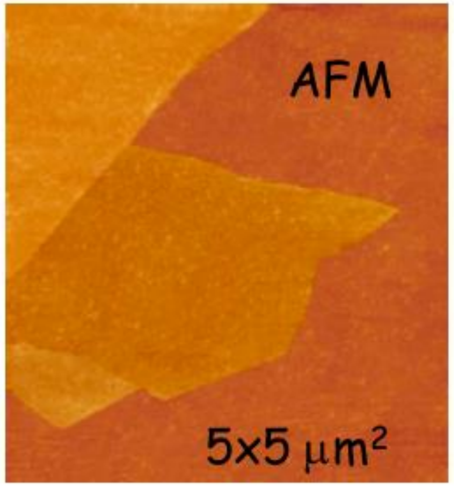


To compare, C_{222} molecule (can be synthesized by chemists)

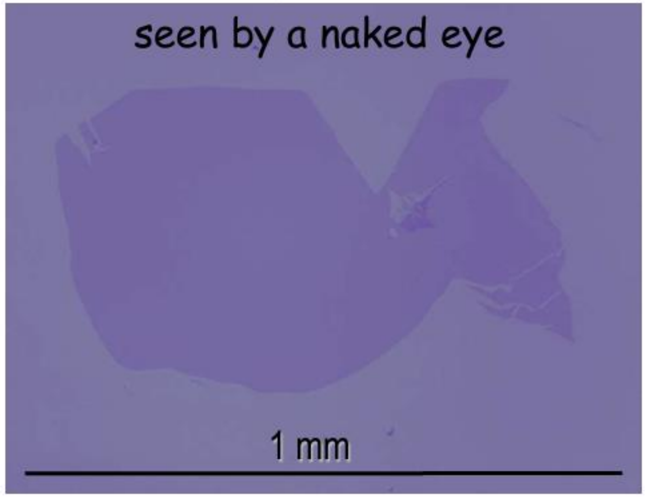




a few years later



a few months later



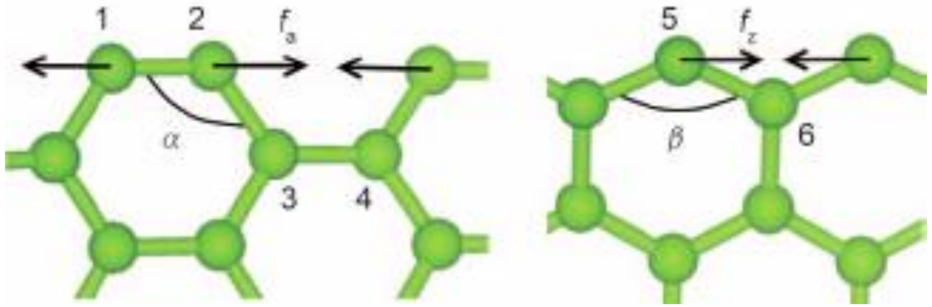
Nobel lecture of A. Geim, 2010, https://www.nobelprize.org/prizes/physics/2010/geim/lecture/

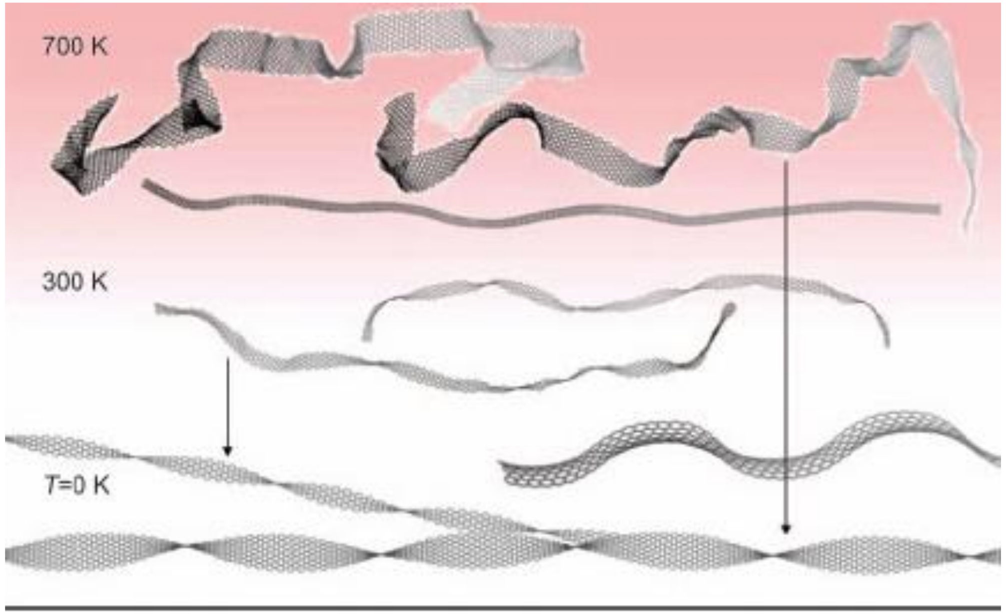
Chem. Rev. 107 (2007) 718

Graphene «twisting» induced by the lower number of bonds at the edges

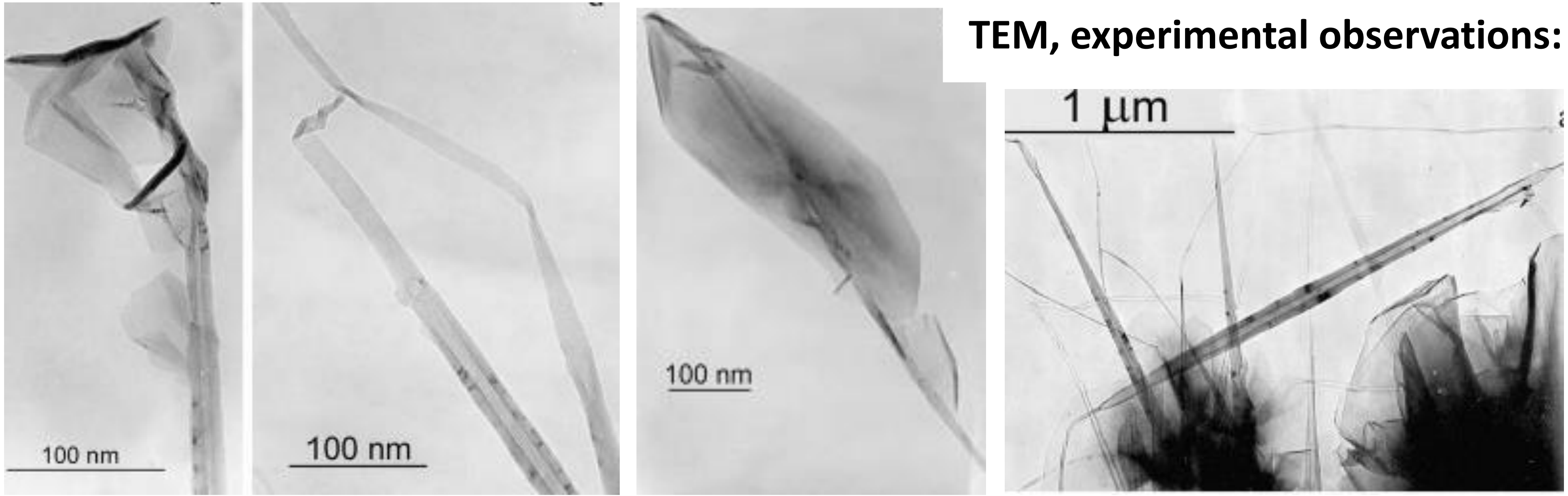
Molecular dynamics, simulation:

Nano Res 2 (2009) 161



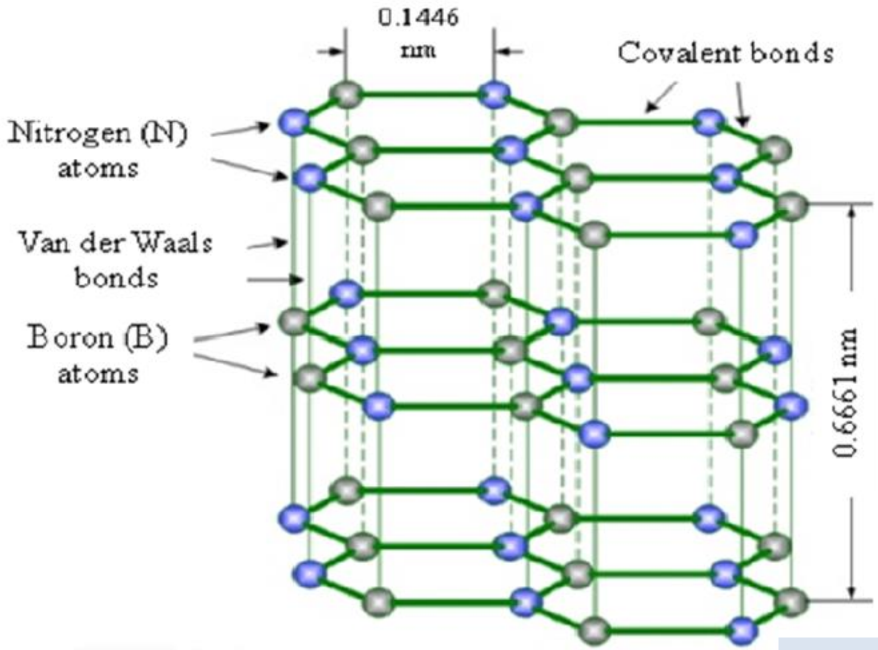


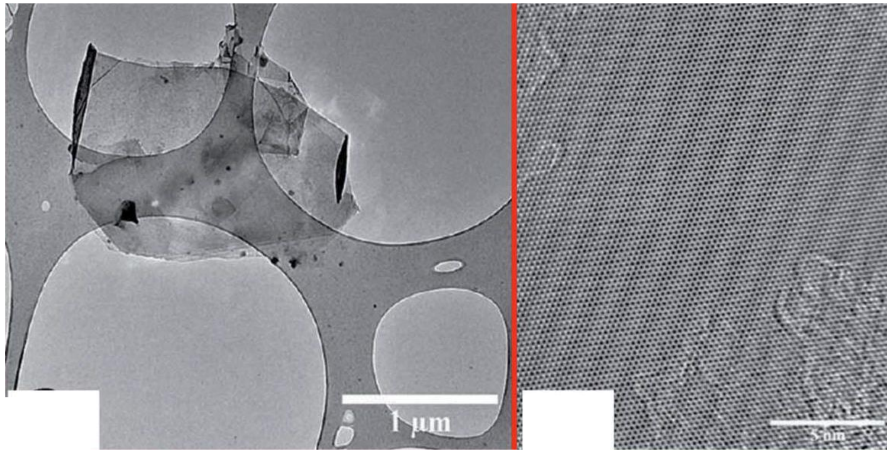
TEM, experimental observations:

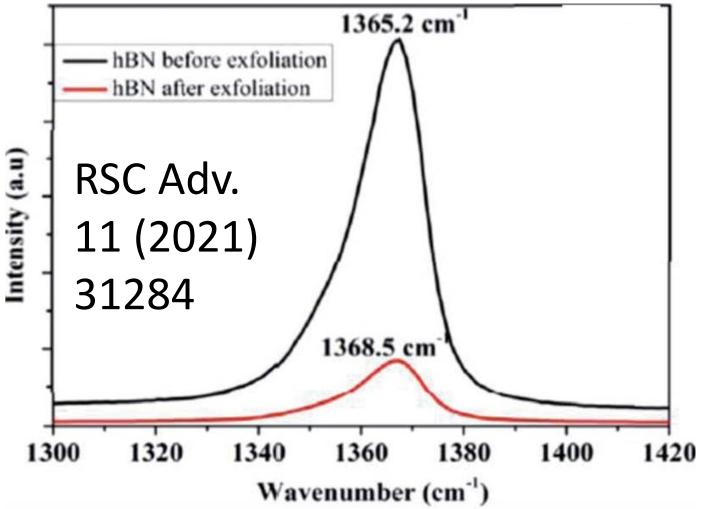


Carbon
47 (2009) 3099

Hexagonal boron nitride (2D insulator), geometry is very similar to graphene

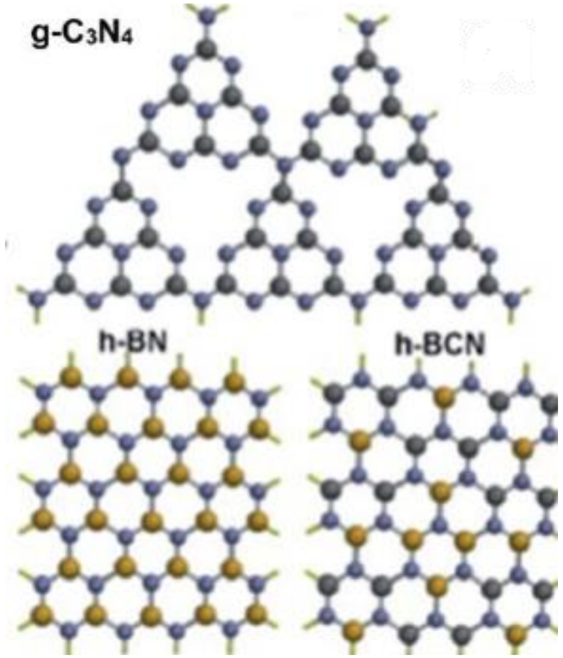




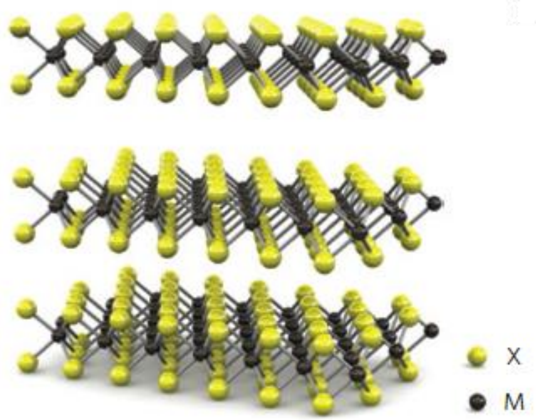


RSC Adv. 11 (2021) 31284

MX_2 compounds (M = metal, X = S, Se, Te)

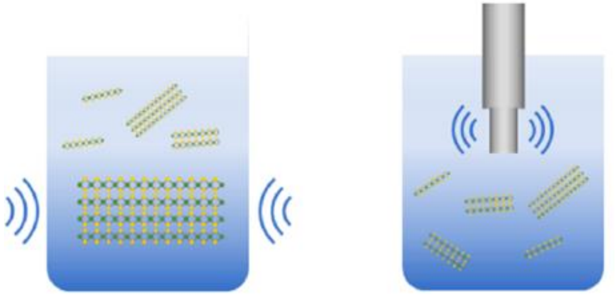


	S	Se	Te
Nb	Metal; superconducting; CDW	Metal; superconducting; CDW	Metal
Ta	Metal; superconducting; CDW	Metal; superconducting; CDW	Metal
Mo	Semiconducting 1L: 1.8 eV Bulk: 1.2 eV	Semiconducting 1L: 1.5 eV Bulk: 1.1 eV	Semiconducting 1L: 1.1 eV Bulk: 1.0 eV
W	Semiconducting 1L: 2.1 eV 1L: 1.9 eV Bulk: 1.4 eV	Semiconducting 1L: 1.7 eV Bulk: 1.2 eV	Semiconducting 1L: 1.1 eV

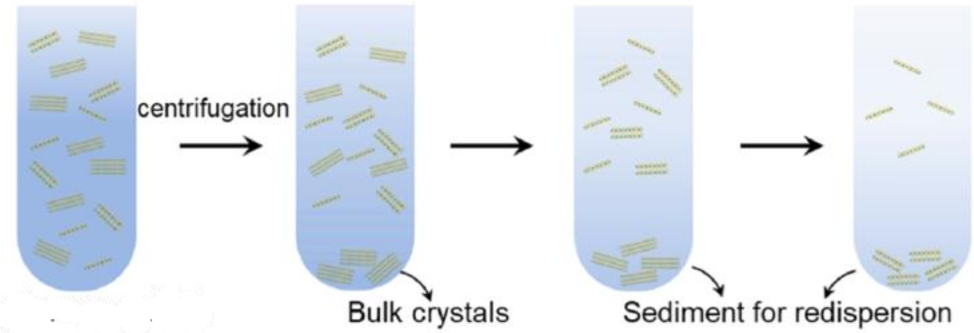


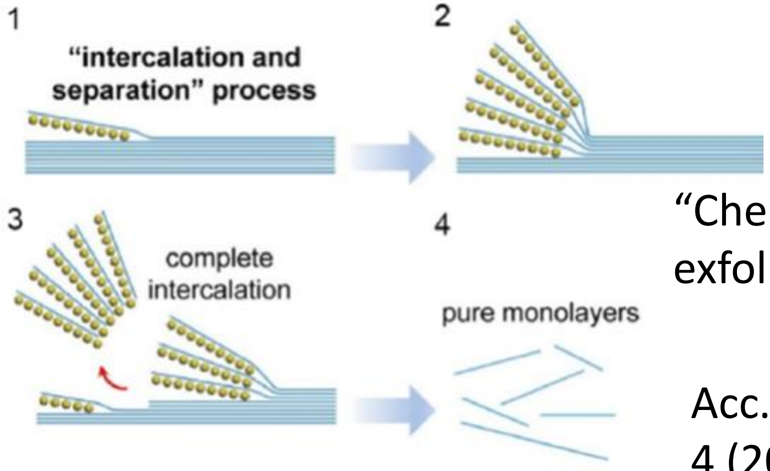
Nature Nanotechnol. 7 (2012) 699

Various possibilities to exfoliate



Ultrasound

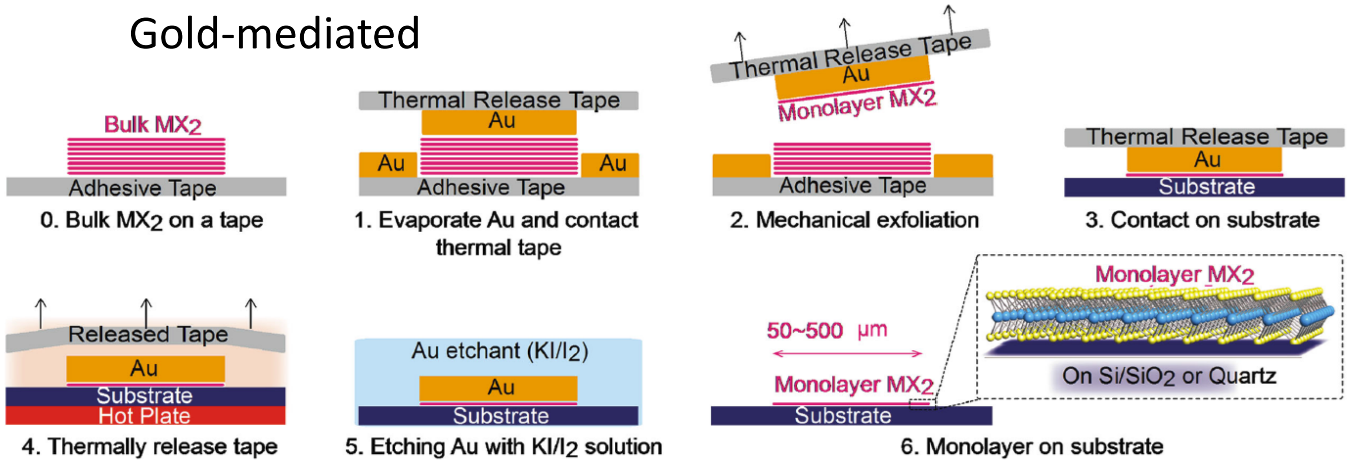


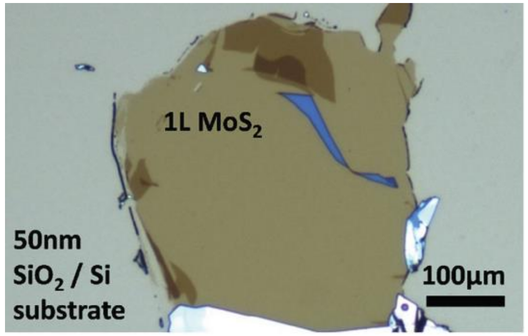


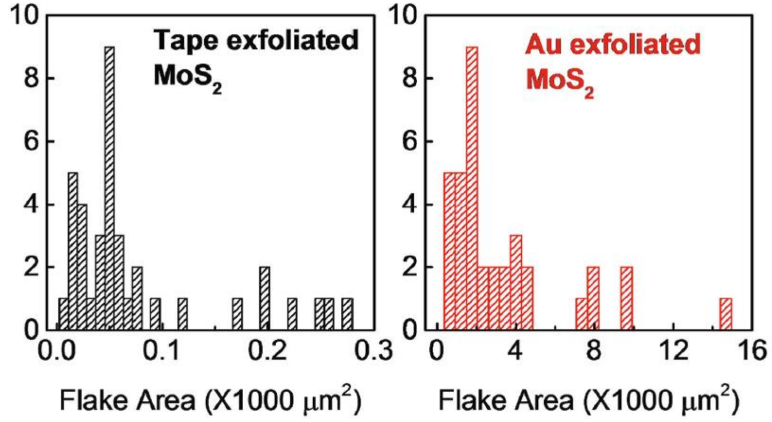
"Chemical" exfoliation

Acc. Mater. Res. 4 (2023) 548−559

Gold-mediated







Adv. Mater. 8 (2016) 4053

There are numerous layered materials with various exfoliation energies, which can be also obtained by CVD.

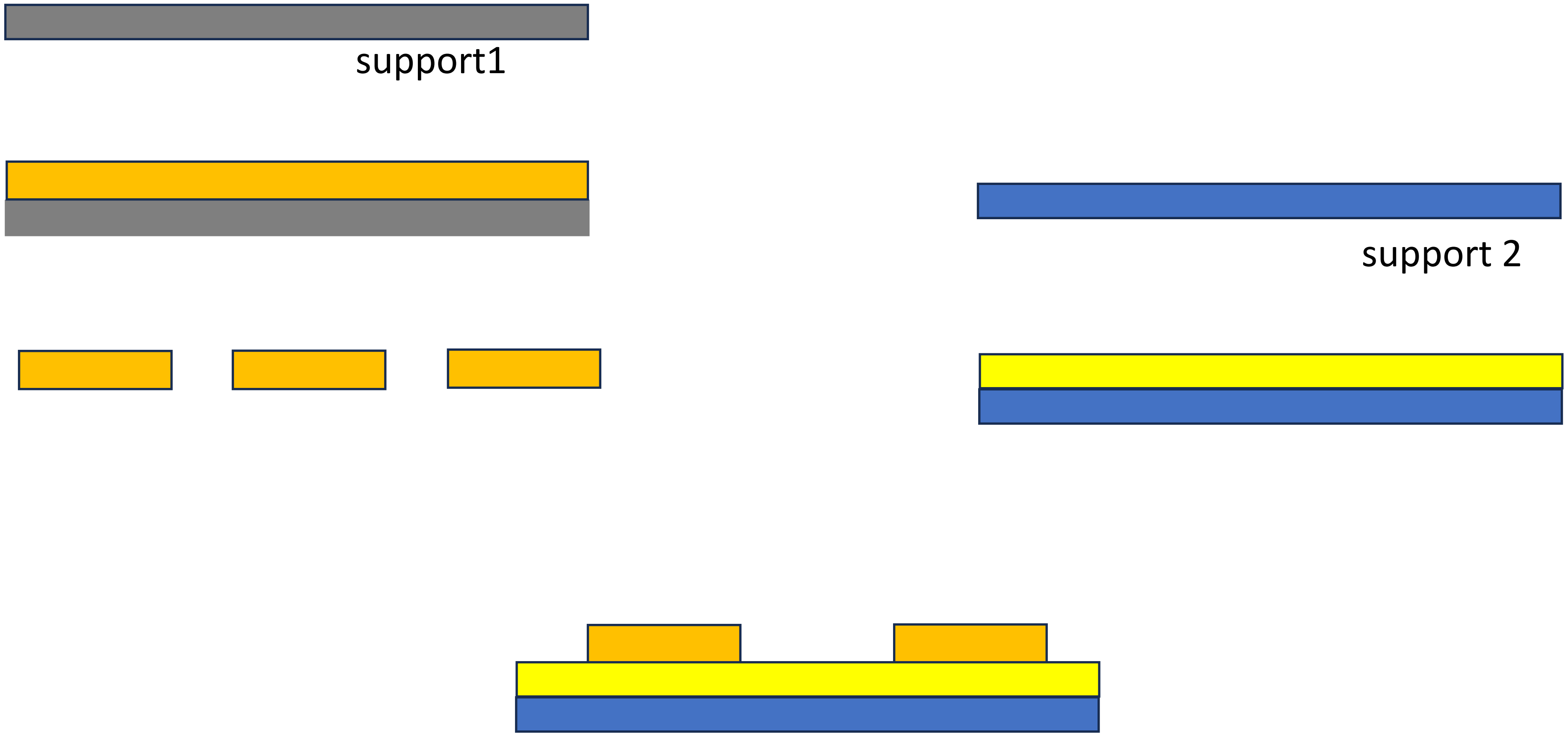
For subsequent and mixed schemes, we need to form 2D films directly on supports.

We can also exfoliate the films to have larger and better quality flakes

Sputtering

or

chemical vapor deposition (CVD)



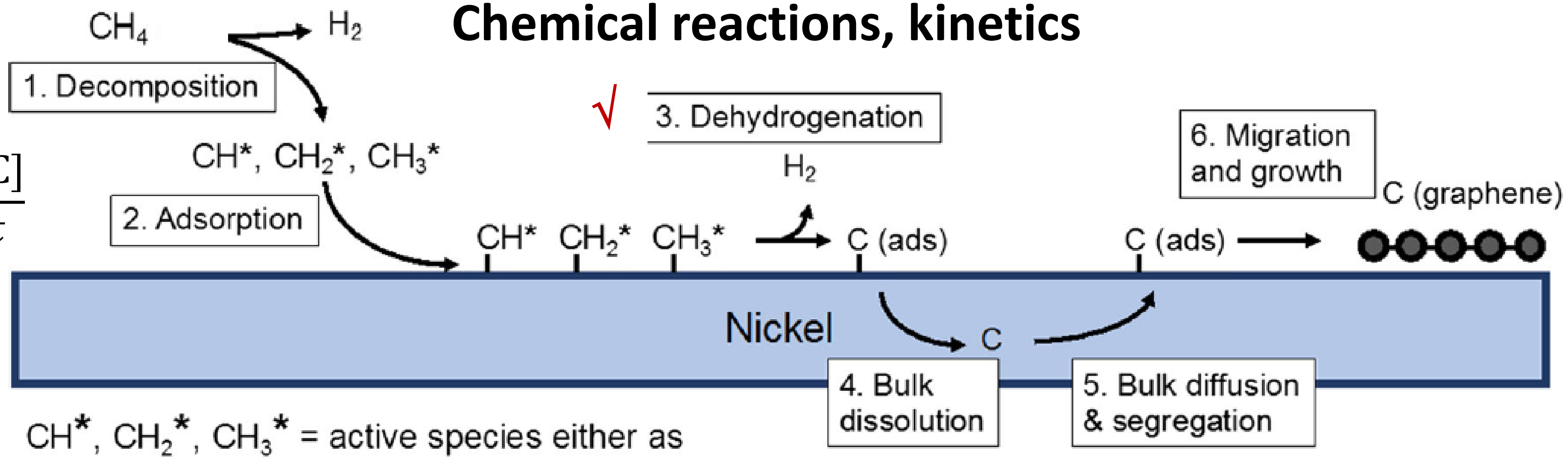
Chemical reactions, kinetics

$\nu_1 A \leftrightarrow \nu_2 B + \nu_3 C$

$$r = -\frac{1}{\nu_1}\frac{d[A]}{dt} = \frac{1}{\nu_2}\frac{d[B]}{dt} = \frac{1}{\nu_3}\frac{d[C]}{dt}$$

observed reaction rate

$$r_{obs} = k(T)[A]^a[B]^b[C]^c$$



CH^*, CH_2^*, CH_3^* = active species either as carbanions or radicals

J. Mater. Sci. 53 (2018) 7095 - 7111

concentrations (in liquid) or
partial pressures (in gas phase);
a, b, c – reaction orders

Pressure and temperature are the most general instruments to control reaction rate in CVD

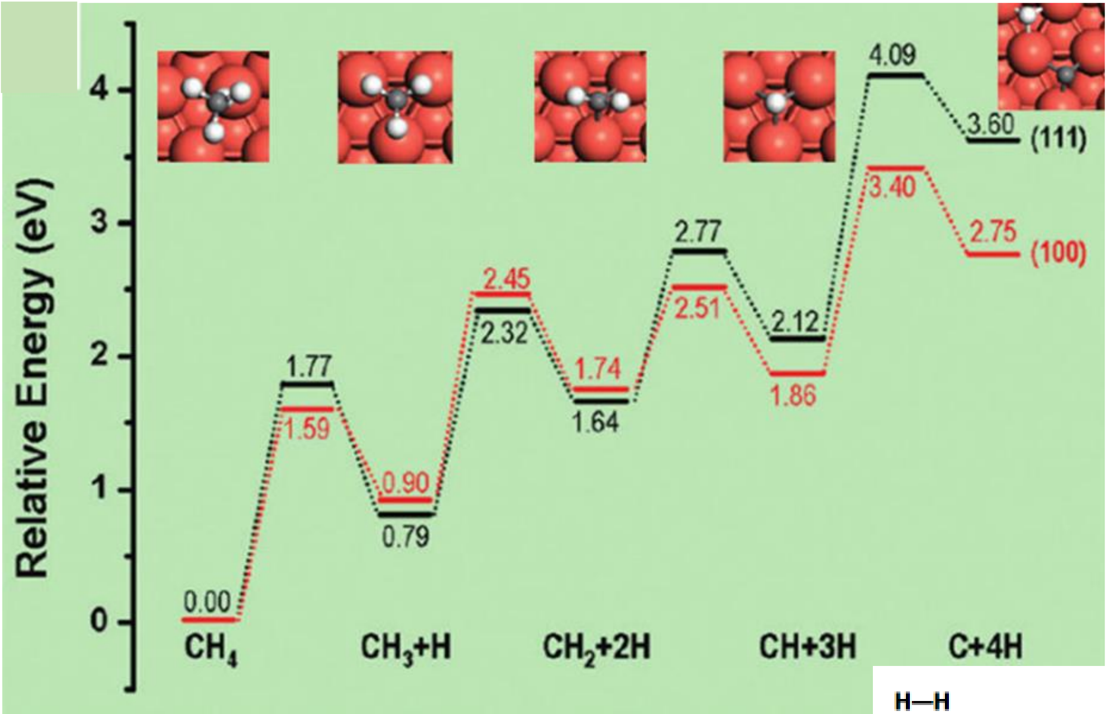
S. Arrhenius

Empiric equation for the rate constant ***k*** of chemical reaction:

$$\frac{d\ln k}{dT} = \frac{E_A}{RT^2}; \quad k = const * \exp\left(-\frac{E_A}{RT}\right)$$

See, e.g., Part 3 of “Physical chemistry” by P. Atkins and J. De Paula

E_A и const are also T-dependent, but their dependencies are weaker than exp.

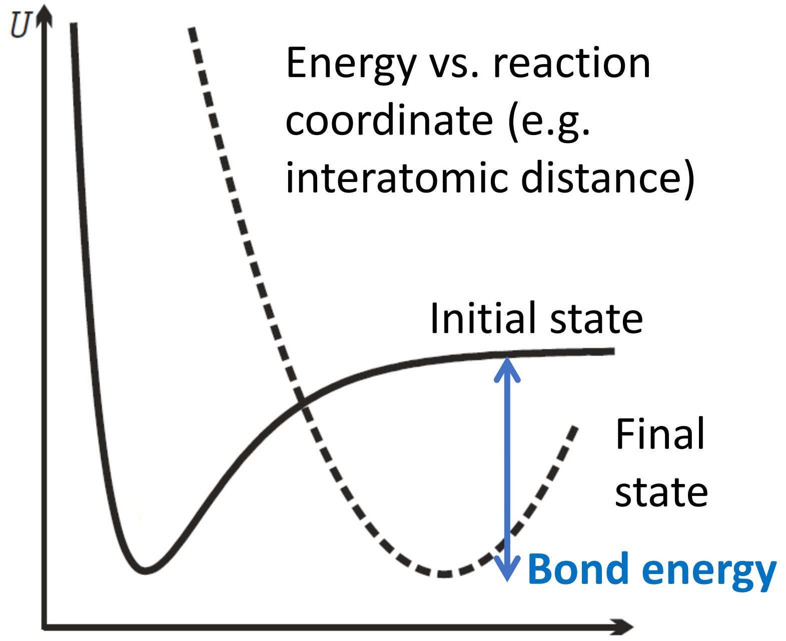


Activation energy results from energy barrier, which can be roughly estimated from quantum chemistry (example for Cu(111) <black> and Cu(100) <red> surfaces

2D Mater. 4 (2017) 042002

For reactions with **bond rupture**, activation energy is more or less close to bond energy.

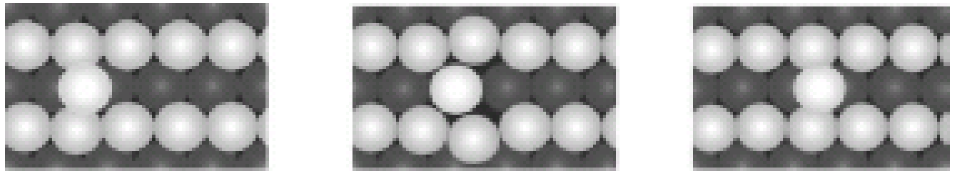
Bond energies, kJ/mol (100 kJ/mol ~ 1 eV)



H—H	432	N—H	391	I—I	149	C = C	614
H—F	565	N—N	160	I—Cl	208	C ≡ C	839
H—Cl	427	N—F	272	I—Br	175	O = O	495
H—Br	363	N—Cl	200			C = O*	745
H—I	295	N—Br	243	S—H	347	C ≡ O	1072
		N—O	201	S—F	327	N = O	607
C—H	413	O—H	467	S—Cl	253	N = N	418
C—C	347	O—O	146	S—Br	218	N ≡ N	941
C—N	305	O—F	190	S—S	266	C ≡ N	891
C—O	358	O—Cl	203			C = N	615

Surface diffusion (migration) step

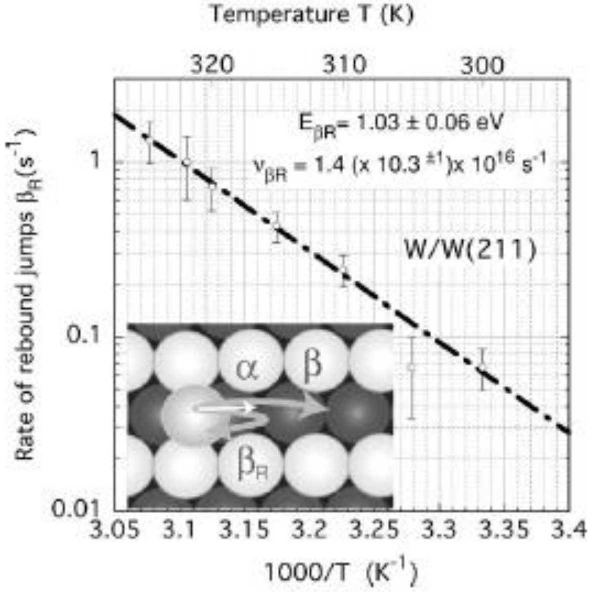
Example of STM visualization (W), 1D surface diffusion



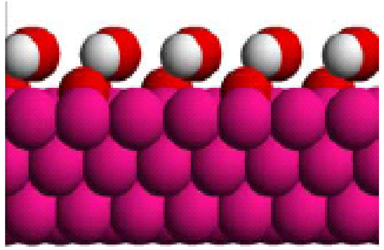
Phys. Rev. B
74 (2006) 153406

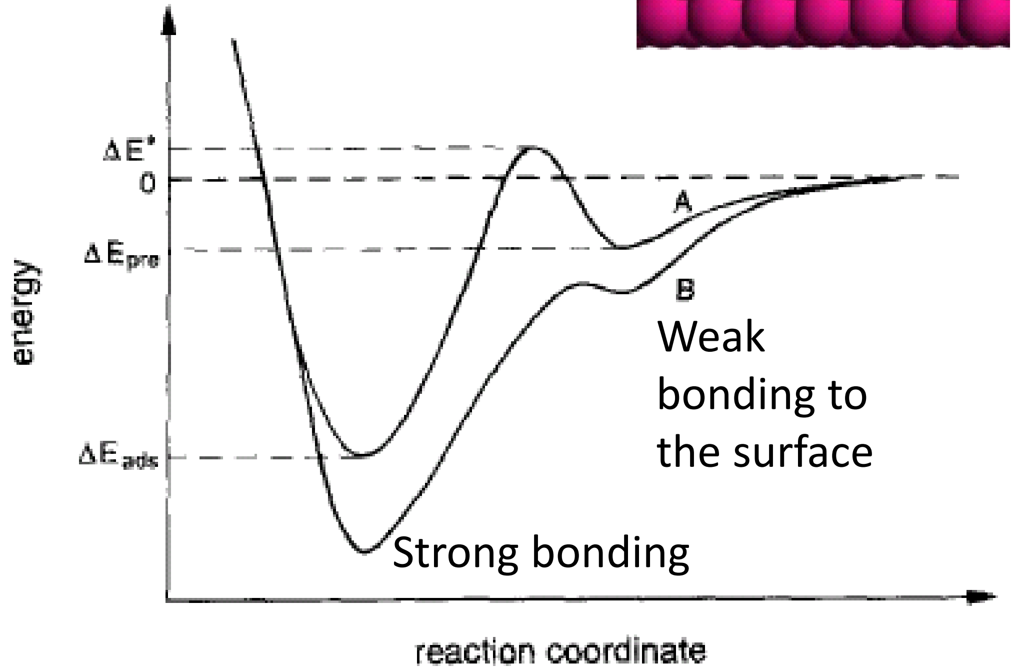
	Activation energy E (eV)	Frequency prefactor ν (s^{-1})
Single jumps α	0.84±0.06	$2.2(\times 11.3^{\pm 1}) \times 10^{13}$
Double jumps β	1.44±0.13	$7.9(\times 127.3^{\pm 1}) \times 10^{21}$
Rebound jumps β_R	1.03±0.06	$1.4(\times 10.3^{\pm 1}) \times 10^{16}$

The rate of surface diffusion roughly corelates with the melting temperature, but also depends on interaction with support.



Adsorption step





Arrhenius behavior is also typical for the rates these steps.

However the surface coverage with adsorbate decreases with temperature.

The principle role of adsorption step is to weaken the bond, to make its rupture easier in the course of subsequent chemical step.

CVD, controlling parameters

Gas pressure

HVCVD ('High Vacuum')

LPCVD (Low Pressure)

APCVD (Atmospheric pressure)

10^{-9} 10^{-6} 10^{-3} 10^{0} 10^{3} log(p, Pa)

Complexity of the reactor is higher for lower pressure, technologically realistic CVD is mostly atmospheric pressure

Temperatures of gas and support

Typical range **- (0.15÷0.30)·t_m**

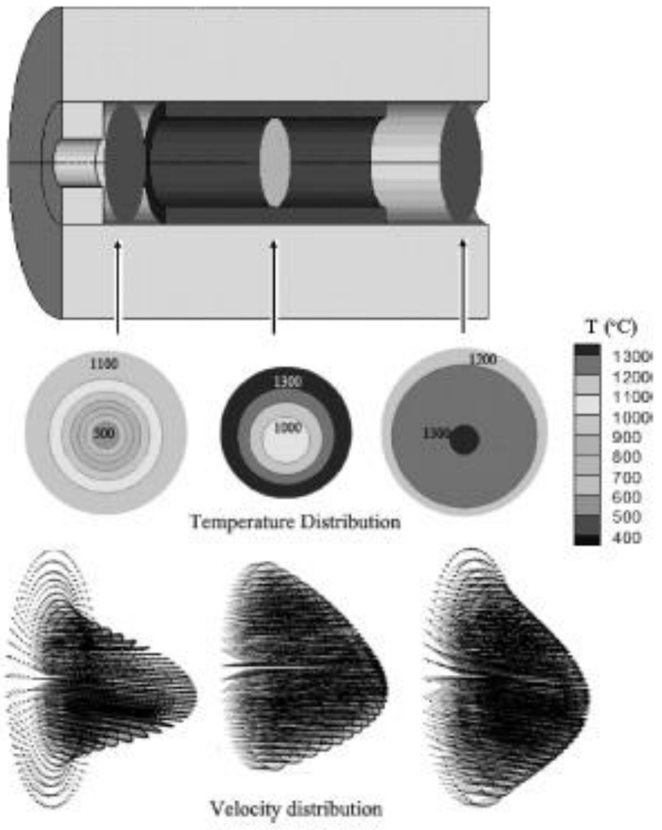
Rapid Thermal (**RTCVD**)

Hot Wire (**HWCVD**) =
= Hot Filament (**HFCVD**)

Dosing of the reagents(s)

Catalysts (cat-CVD)

Reactor configuration (Source – support distance)



Additional controlling parameters + temperature decrease:

Plasma Enchanced (**PECVD**)

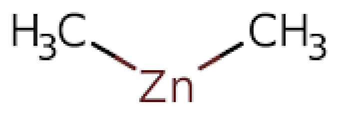
Plasma Assisted (**PACVD**); Microwave Plasma-Assisted (**MAPCVD**)

Laser Assisted CVD

Old-fashioned MOCVD precursors for III-V and II-VI binary semiconductors

Compound	Symbol	Melting point (°C)	Boiling point at 760 mm (°C)	Vapor pressure (mm)
Dimethylzinc	DMZn	−42 (−29)	46	124 at 0°C
Diethylzinc	DEZn	−28	118	15 at 20°C
Dimethylcadmium	DMCd	−4.2	105.5	350 at 80°C
Trimethylaluminum	TMAl	15.4	126	8.4 at 20°C
Trimethylgallium	TMGa	−15.8	55.7	64.5 at 0°C
Triethylgallium	TEGa	−82.3	143	18 at 48°C
Diethylgalliumchloride	DEGaCl	—	—	—
Trimethylindium	TMIn	88.4	135.8	7.2 at 30°C
Triethylindium	TEIn	−32	184	3 at 53°C
Tetramethyltin	TMSn	−53	78	10 at −20°C
Tetraethyltin	TESn	−112	179.5–181.5	10 at 73°C
Tetramethyllead	TMPb	−27.5	110	10 at 4.4°C
Tetraethyllead	TEPb	−135	198–202	10 at 78°C
Triethylphosphine	TEP	−88 (−85)	127	—
Trimethylantimony	TMSb	−87.6 (−62.0)	80.6	—
Dimethyltelluride	DMTe	−10 (−150)	82 (93.5)	—
Diethyltelluride	DETe	—	137–138	—

Ann. Rev. Mater. Sci. 12 (1982) 243-269



Angew. Chem. Int. Ed. 50 (2011) 11685

All these compounds contain metal-carbon bond, long enough (ca. 2 A), and its with bond energies of 1.5 – 3 eV.

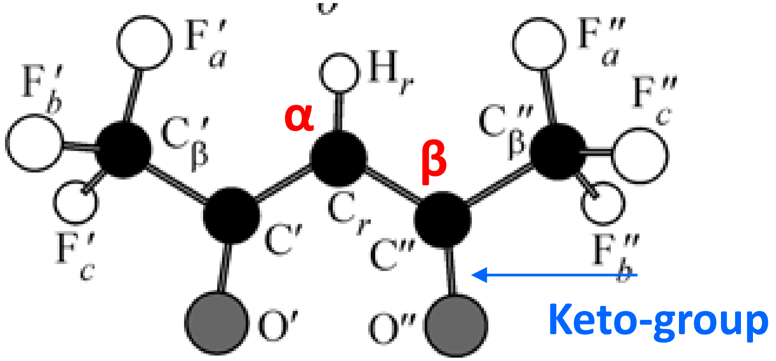
Metal-organic CVD (MOCVD), precursors

1

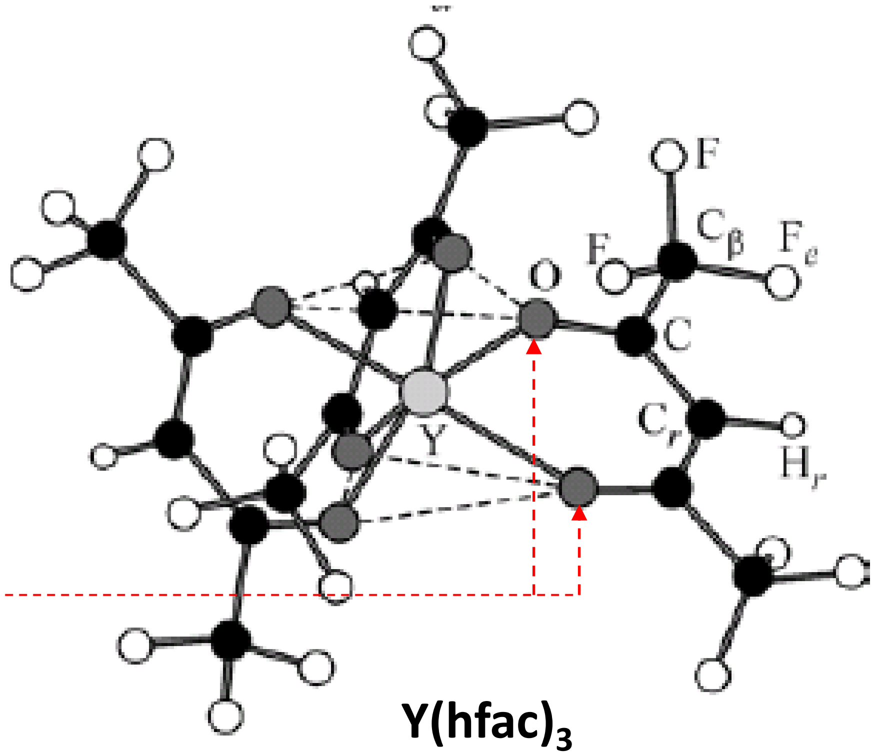
- low band polarity
- low ligand polarization
- not so large molecule
- minimal ligand-ligand interactions

→ **Volatility**

β-diketonates



β-hexafluoroacetylacetonate, hfac)



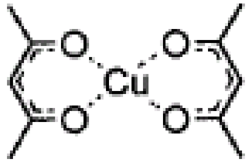
$Y(hfac)_3$

2 **Optimal metal-ligand bond energy:**

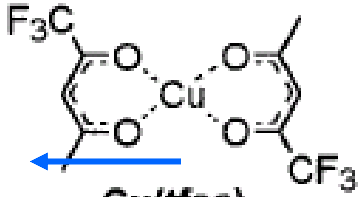
- stability under evaporation
- easy bond rapture

3 **Ability to absorb on the support**

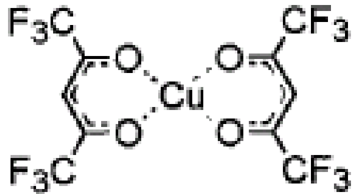
Copper CVD precursors: peripheral groups affect volatility



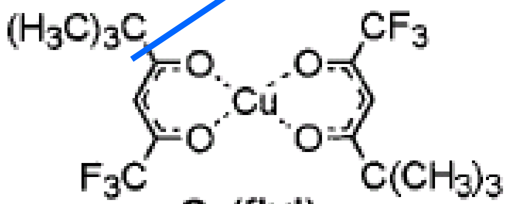
$Cu(acac)_2$



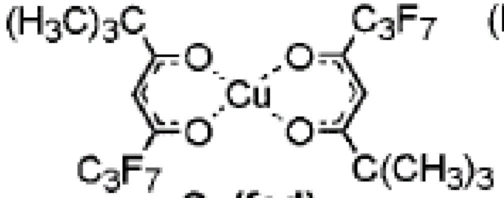
$Cu(tfac)_2$



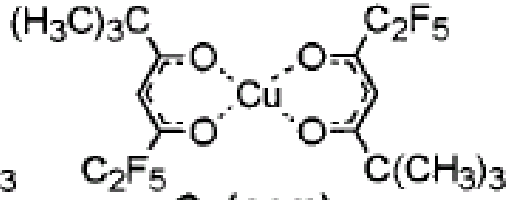
$Cu(hfac)_2$



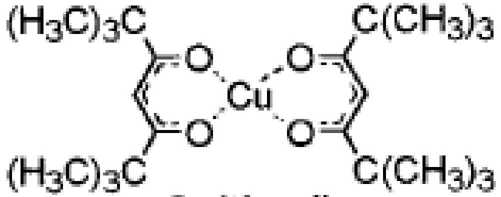
$Cu(fhd)_2$



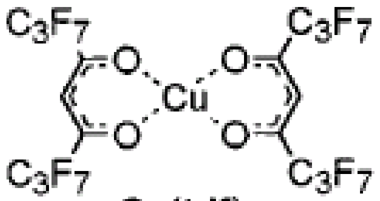
$Cu(fod)_2$



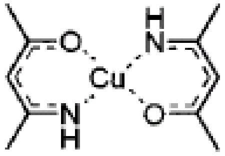
$Cu(ppm)_2$



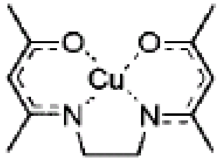
$Cu(thmd)_2$



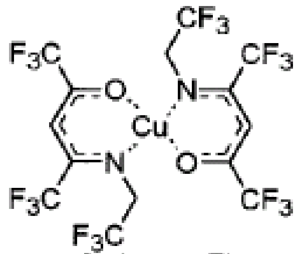
$Cu(tdf)_2$



$Cu(acim)_2$



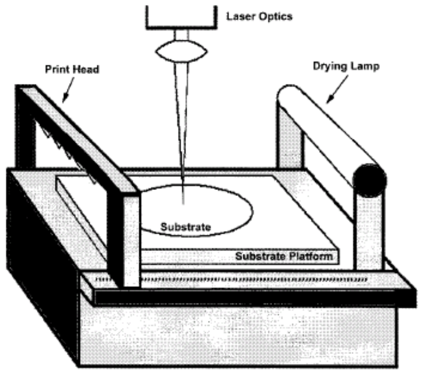
Cu(acen)



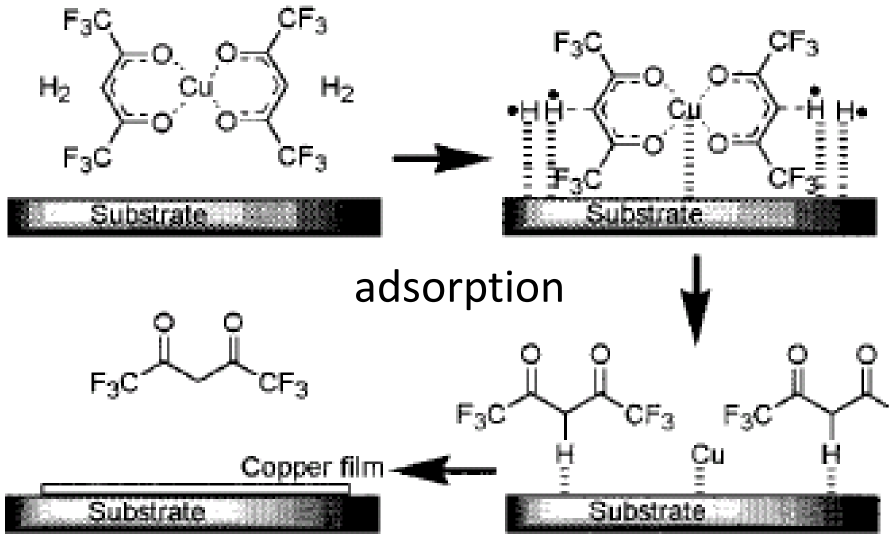
$Cu(nona\text{-}F)_2$

precursor	evaporation temp (°C)
$Cu(hfac)_2$	120
$Cu(tfac)_2$	135–160
$Cu(acac)_2$	180–200
$Cu(thmd)_2$	100
$Cu(ppm)_2$	100
$Cu(fod)_2$	-
$Cu(acim)_2$	287
Cu(acen)	204
$Cu(nona\text{-}F)_2$	85–105

$p \ll 1$ atm



CVD-printing (1 – 400 μm)



adsorption

reaction

by-product removal

Chem. Rev. 102 (2002) 1525-49

Ultraviolet-assisted injection liquid source CVD (UVILS-CVD)

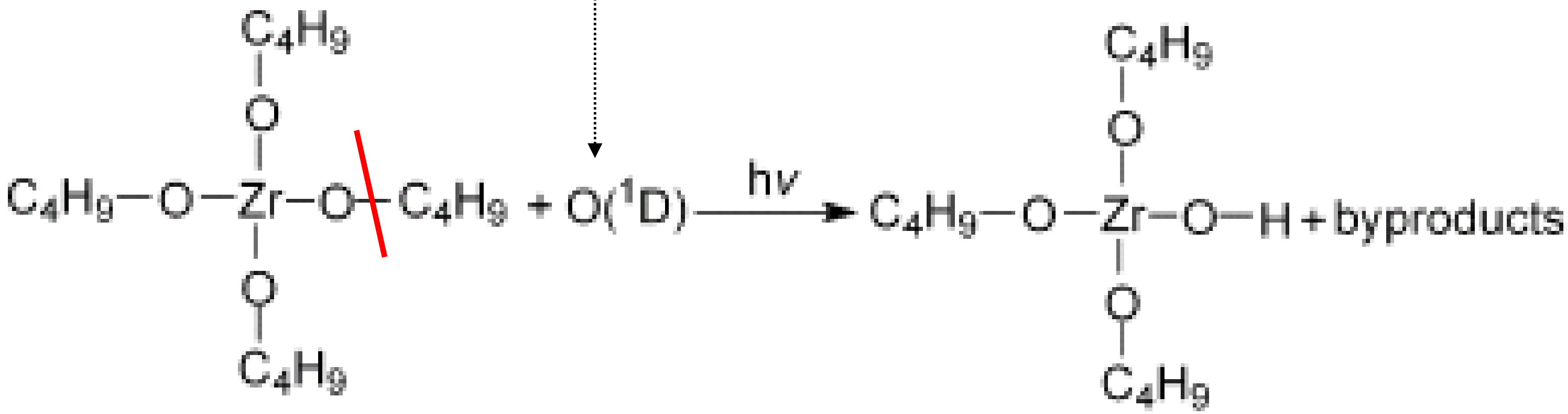
$Zr[OC(CH3)_3]_4 + N_2O \rightarrow ZrO_2 + N_2$

Zirconium oxide is material with O^{2-} ionic conductivity, it is a basic material for solid electrolytes.

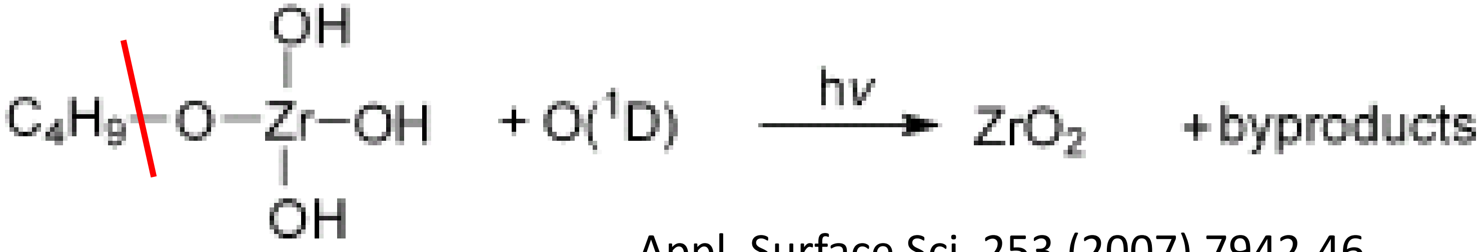
N_2O is the precursor of **oxidizer**, which **is O radical** resulting from N_2O photodecomposition;

light intensity regulates the amount of oxidizer.

$$N_2O \xrightarrow{h\nu} O(^1D) + N_2(X^1\Sigma_g^+)$$

1.


….. Subsequent oxidation of other butyl groups……

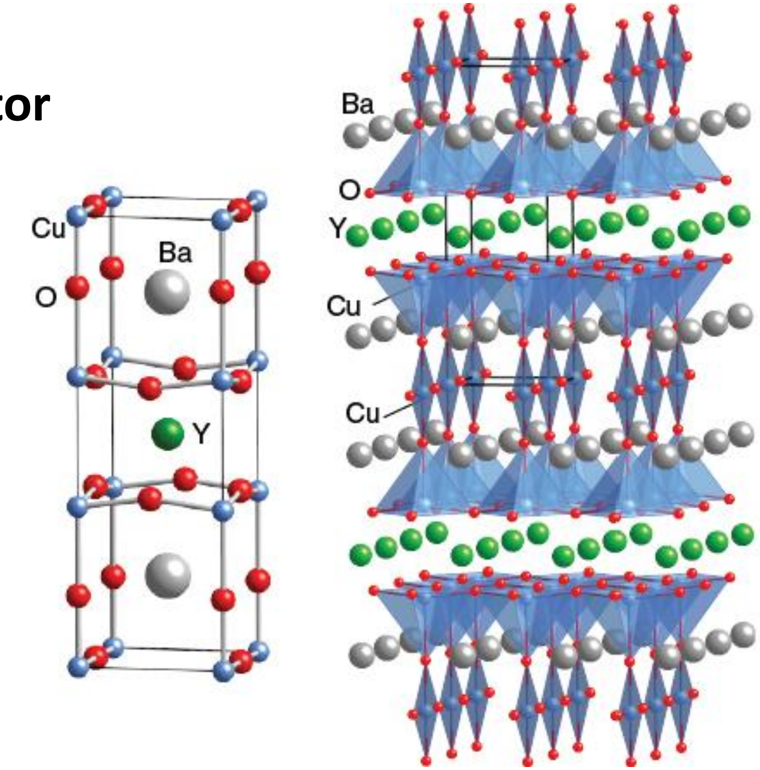
4.


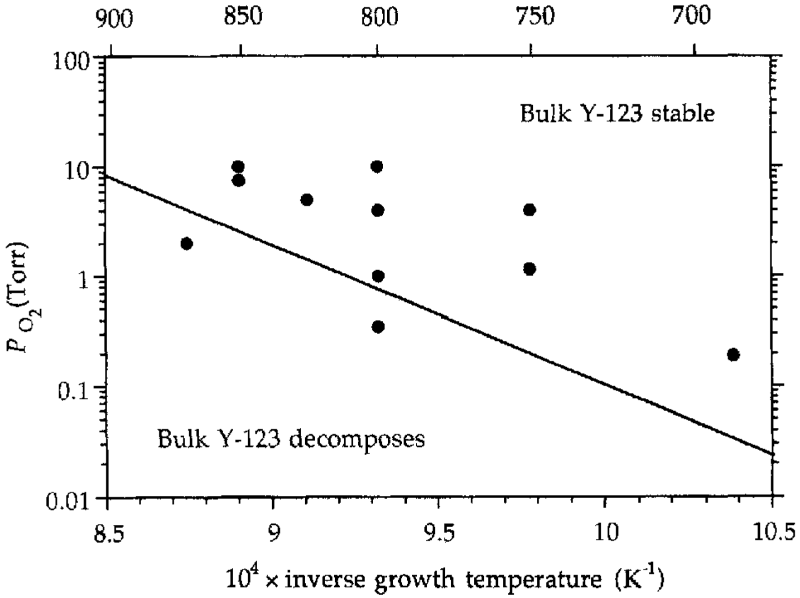
Appl. Surface Sci. 253 (2007) 7942-46

Multisource CVD

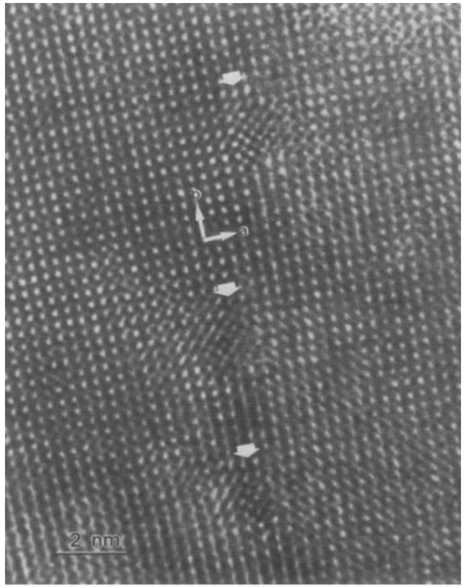
High temperature superconductor (HTSC), $YBa_2Cu_3O_{6.5+x}$ or $YBa_2Cu_3O_{7-x}$

(also named “1-2-3”)





Chem. Vap. Deposition 3 (1997) 9-26



PhysicaC 174 (1991) 1

Crystallographic orientation

Low-angle boundaries ⟷

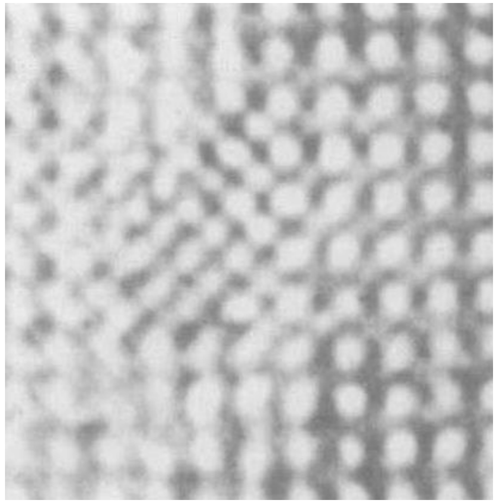
Oxygen nonstoichiometry

Precursor evaporation:
- **total pressure**
- **flow rate**

Oxidizer pressure

Y, Ba, Cu dosing

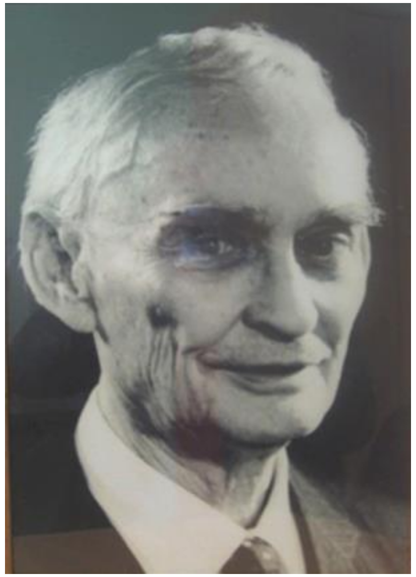
Temperature

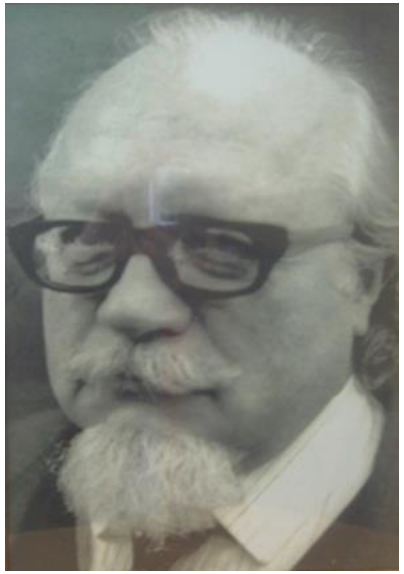


Precise morphology, epitaxial deposition

Single-source CVD

Up to 100 nm/min,
but incomplete surface coverage





V. B. Aleskovskii **S. I. Kol'tsov**

Repeated self-terminated reactions (reagent is provided under pulse mode)

→ **Atomic Layer Deposition (ALD)** or **Atomic Layer Epitaxy (ALE)** or **Molecular Layering**

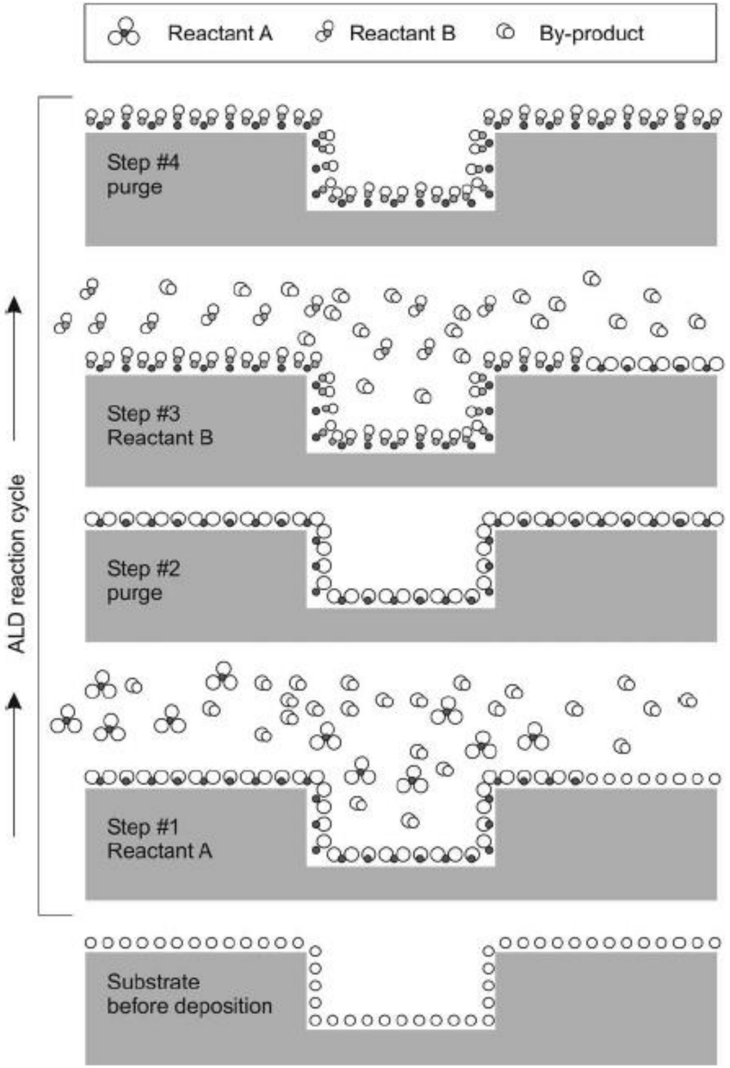
T. Suntola

Multisource CVD, pulse mode

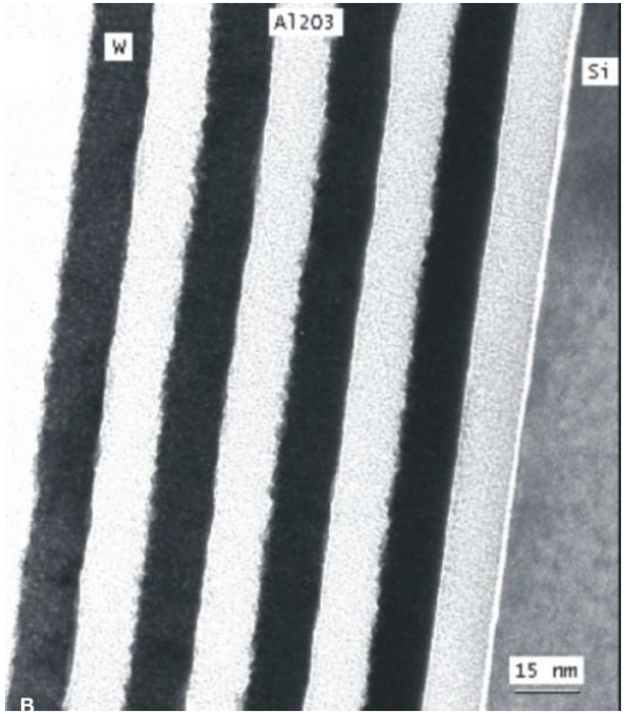
Single crystalline well-defined supports

Rotating supports

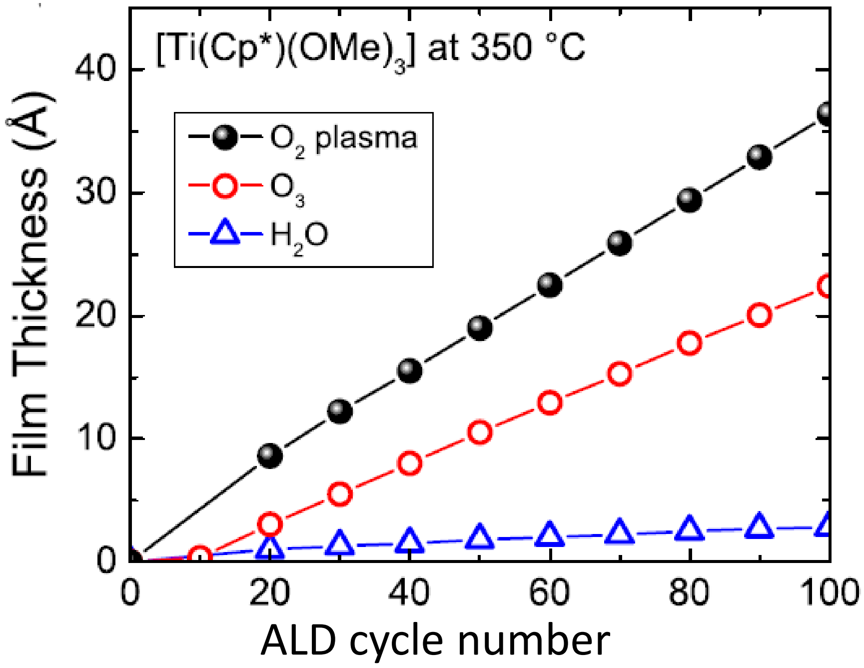
Very slow, up to ~1 nm/min



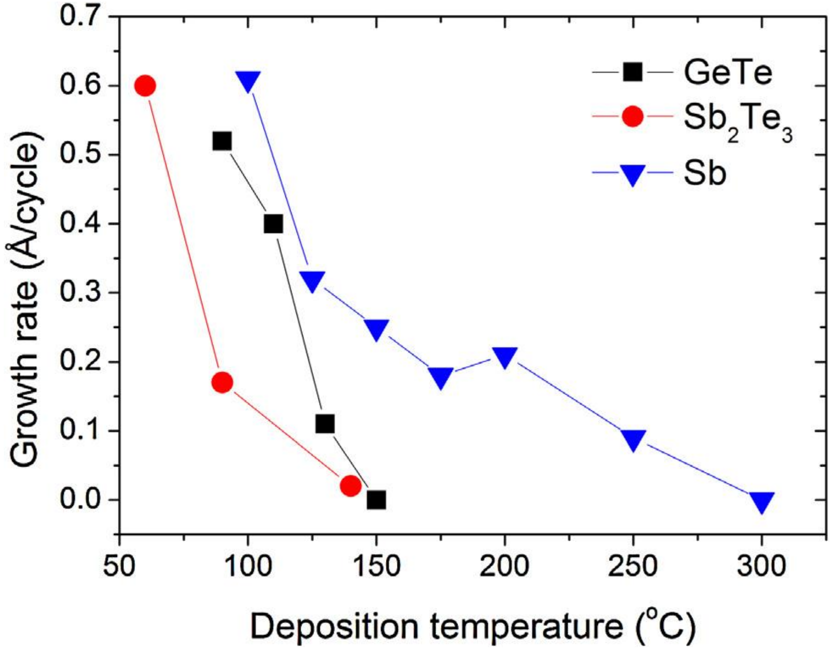
J. Appl. Phys. 97 (2005) 121301



Chem.Mater. 17 (2005) 3475

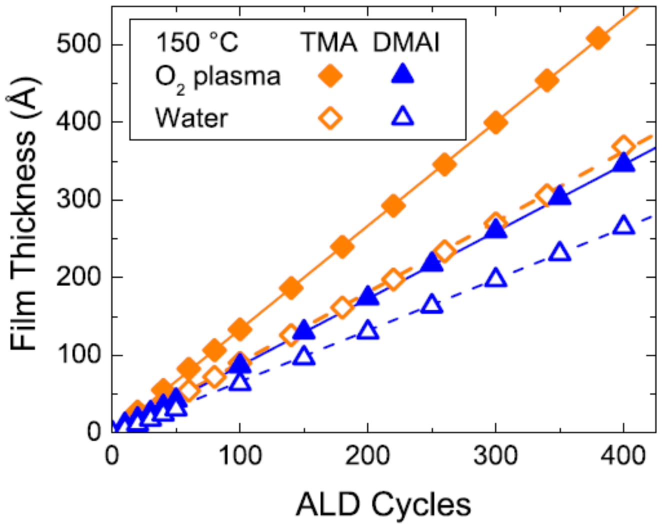


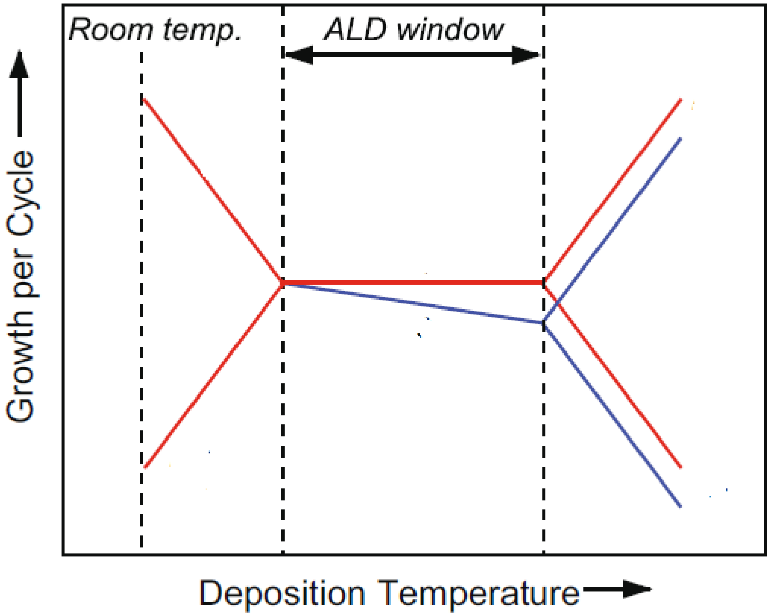
Coord. Chem. Rev. 257 (2013) 3254

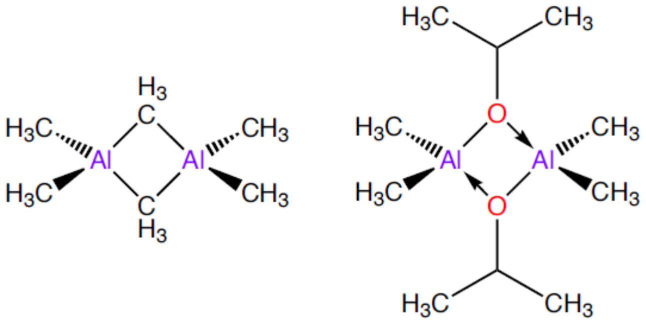


Coord. Chem. Rev. 257 (2013) 3297

To keep growth rate approximately the same in each cycle, and also not too low, intermediate temperatures are required ("ALD window").

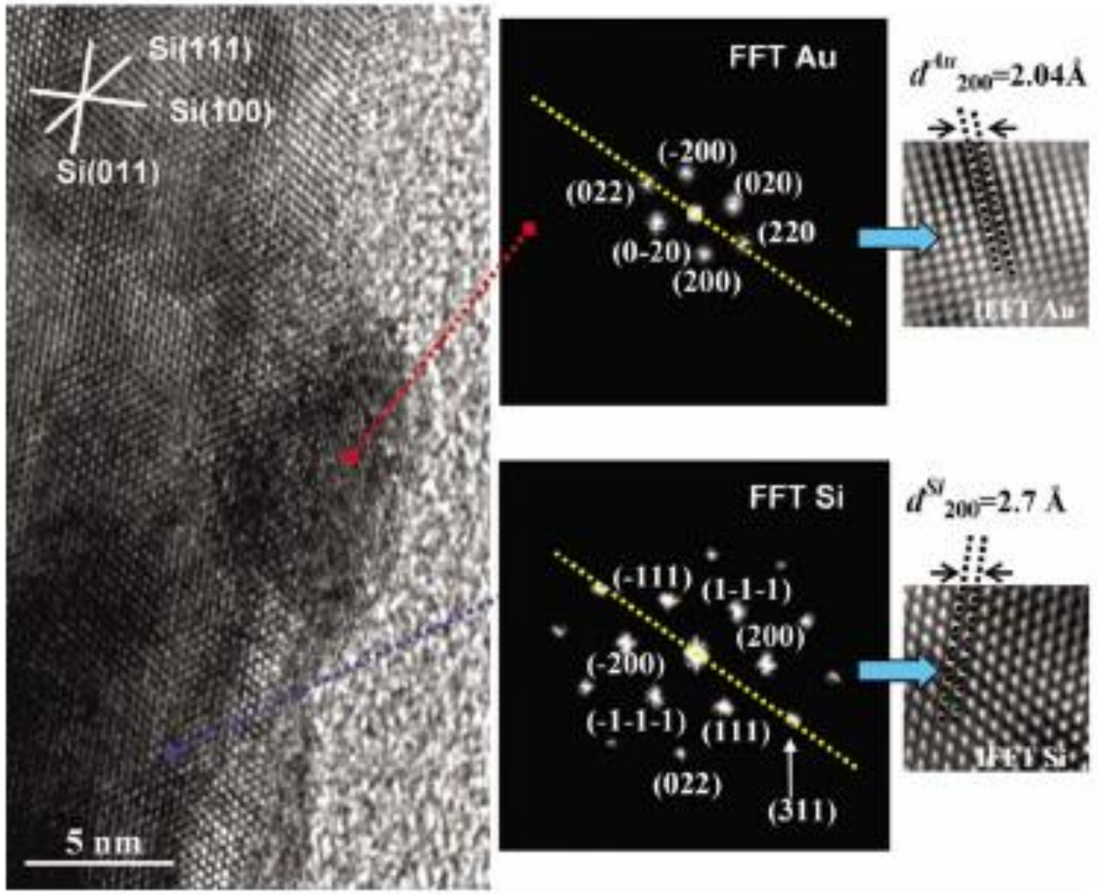


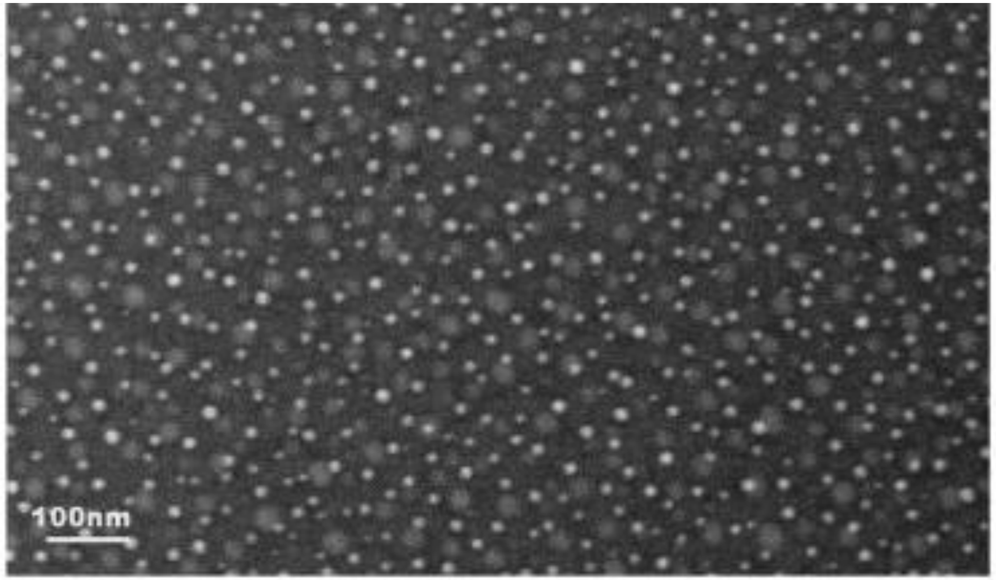




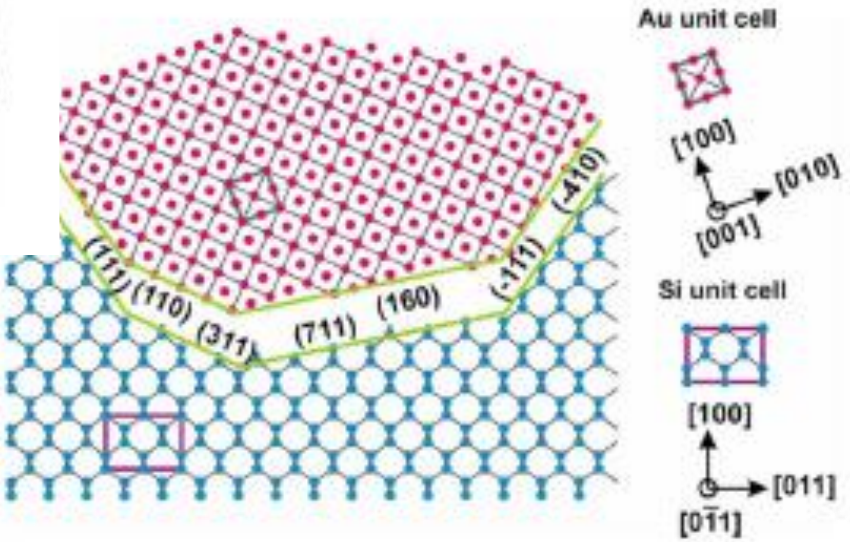
TMA DMAI

Epitaxial growth in case of pronounced lattice mismatch





Si on Au, 25% difference in lattice parameters

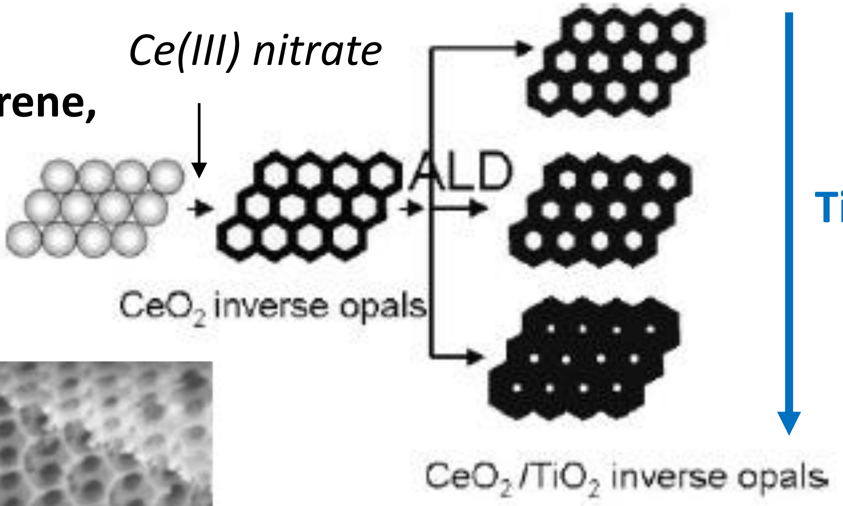


Phys. Rev. B 78 (2008) 035305

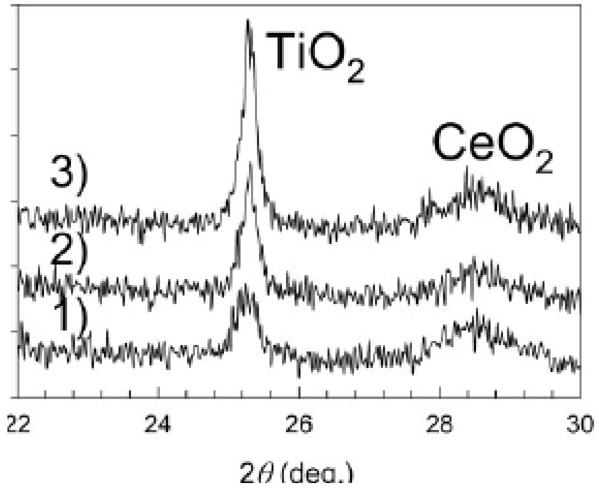
ALD at non-planar interface: CeO_2/TiO_2 photonic crystals

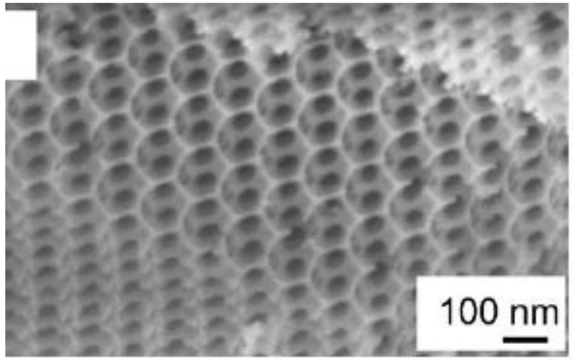
Ce(III) nitrate

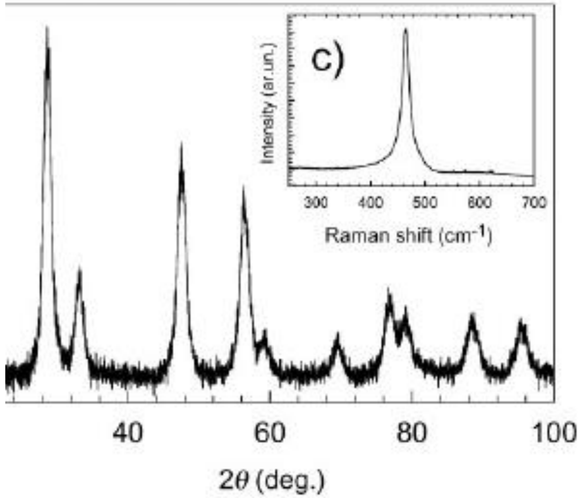
Polystyrene, 150 нм

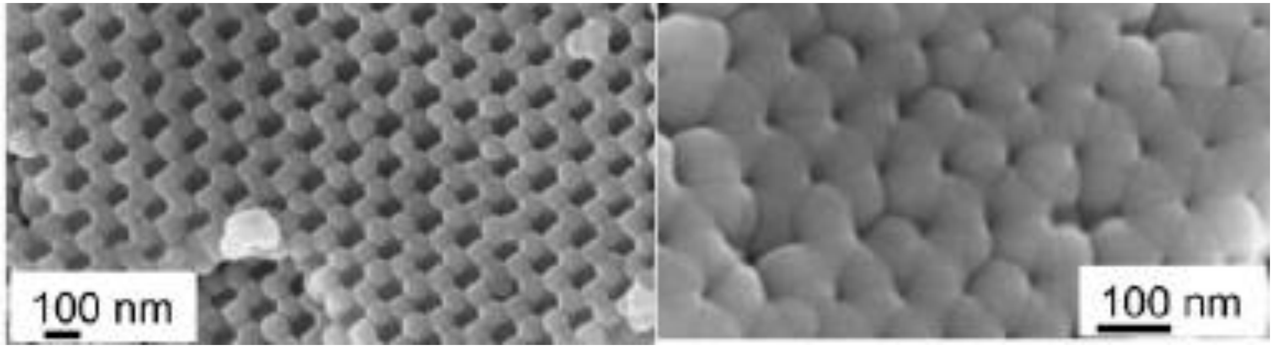


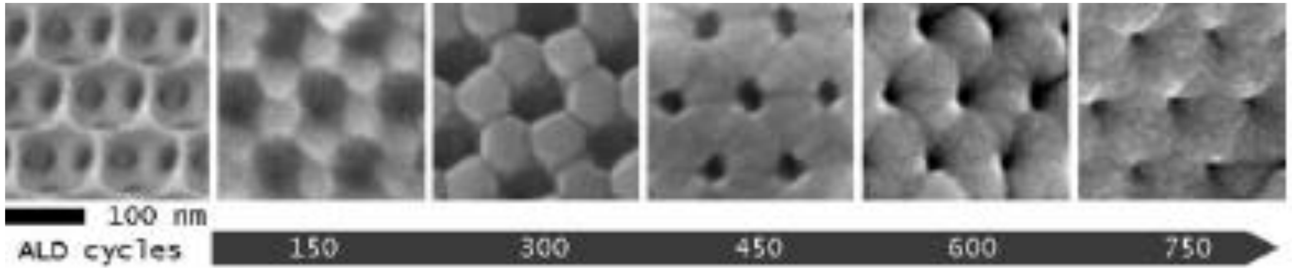
TiO_2 ALD cycles











Small 5 (2009) 336-340

2D material: books and reviews on CVD and epitaxial deposition

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