Fabrication of nanostructures and nanoscale devices.
Part 4.

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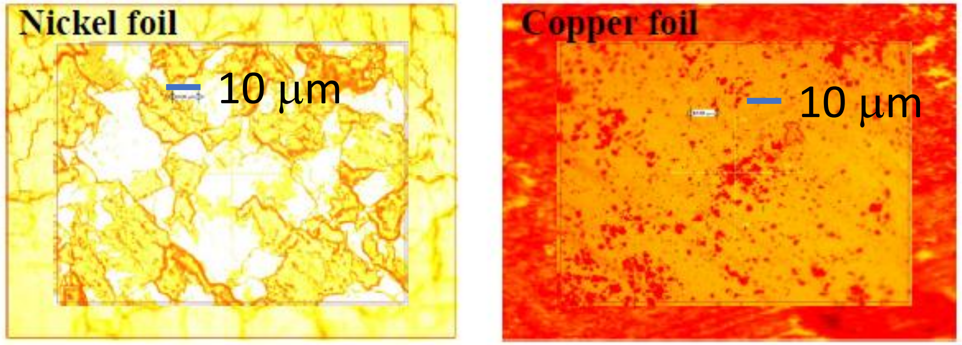
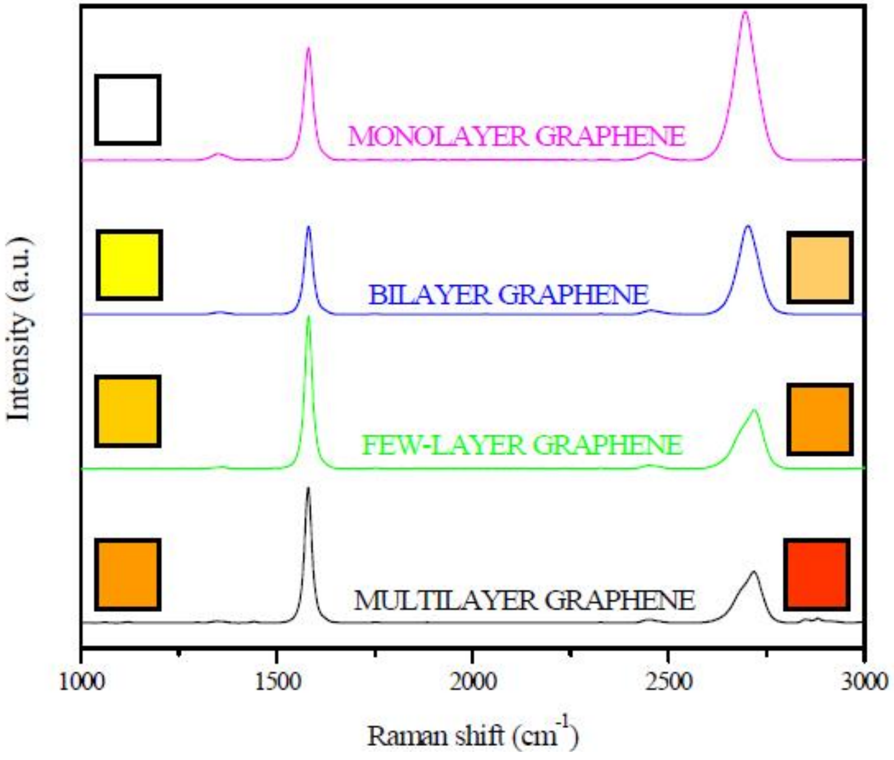
See the lectures at https://www.nanocenter.si/qt-future/education-2/

How to distinguish a single layer regions in 2D flakes?

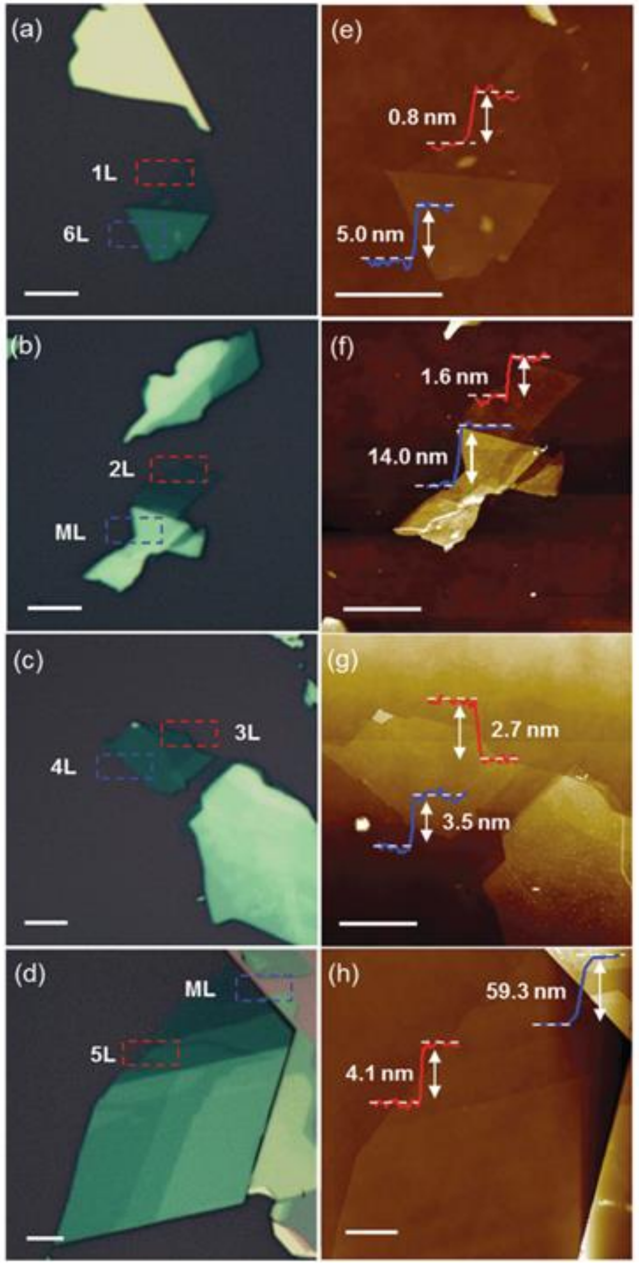
Q3

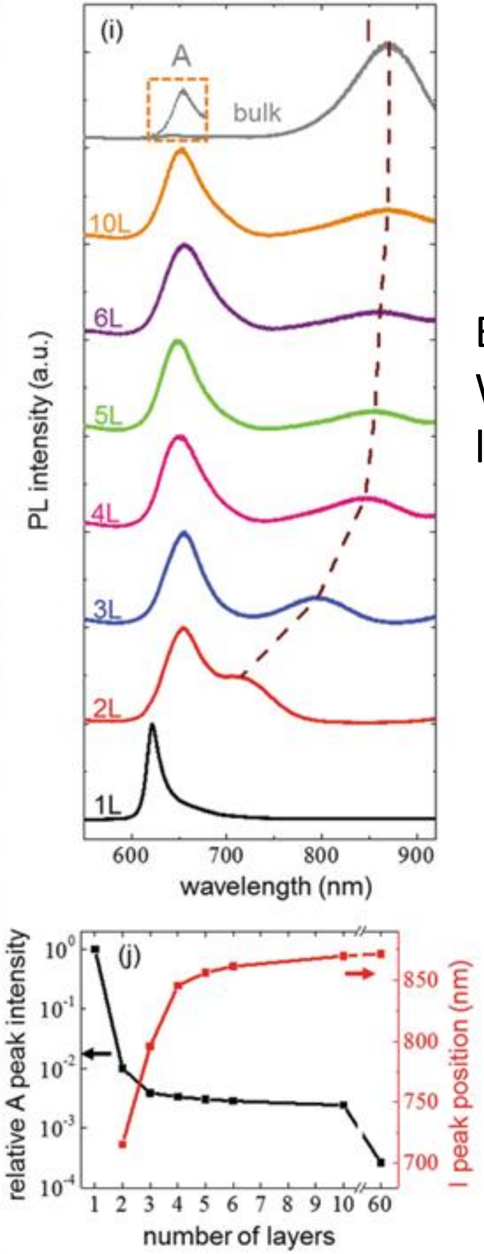


CVD graphene grown on Ni and Cu, Raman



AIMS Mater. Sci. 4 (2016) 194





Exfoliated WS2, luminescence

Mater. Horiz. 6 (2019) 97

Parts 3-4, Outline

Fabrication of Thin Films (2D fragments of nanostructures)

Part 3

- 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))

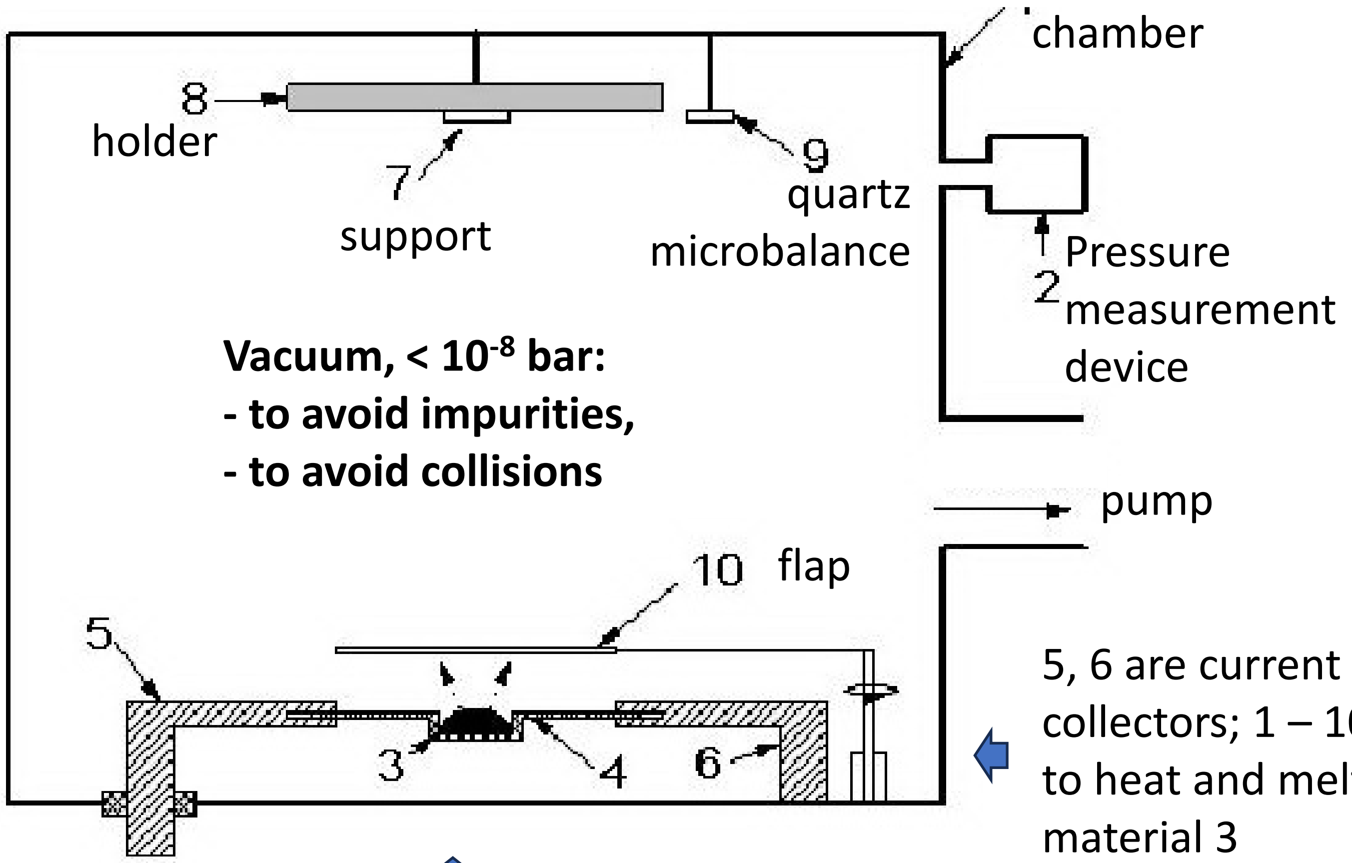
Part 4

- Physical vapor deposition (thermal, laser, magnetron; growth control and monitoring)

- Wet deposition (electroless)

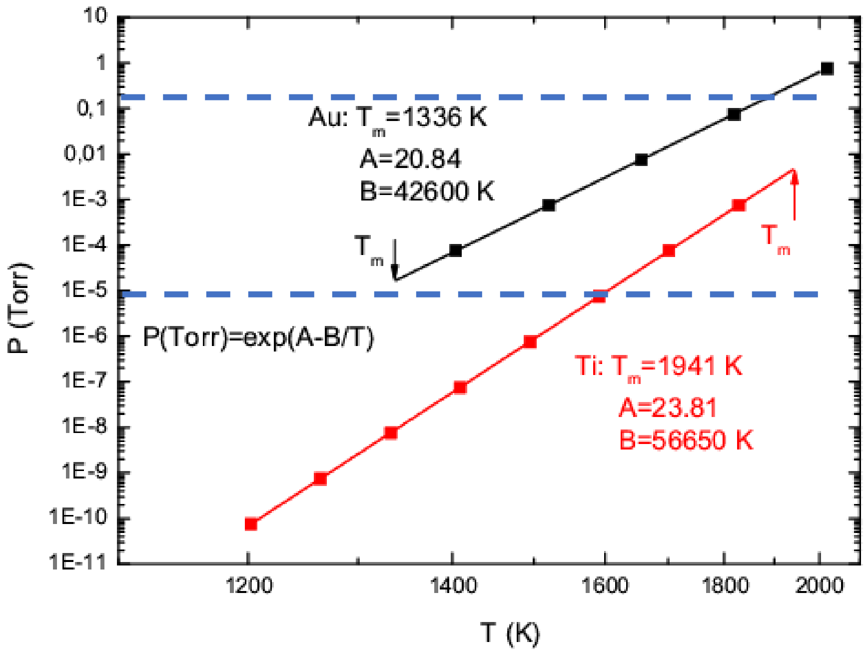
- Wet deposition (electrochemical)

Thermal sputtering (evaporation)



Vacuum, < 10^{-8} bar:
- to avoid impurities,
- to avoid collisions

5, 6 are current collectors; 1 – 10 A to heat and melt material 3



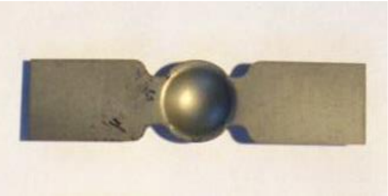
Equilibrium vapor pressure, examples for gold and titanium; typical values for evaporation are ~10^{-5}–10^{-1} Torr (~10^{-8}–10^{-4} bar)

evaporation rate:

$$\frac{dm}{dt} = P(T_{ev})\sqrt{\frac{m_a}{2\pi k T_{ev}}}$$

atomic mass

«boat» 4 for evaporating material 3

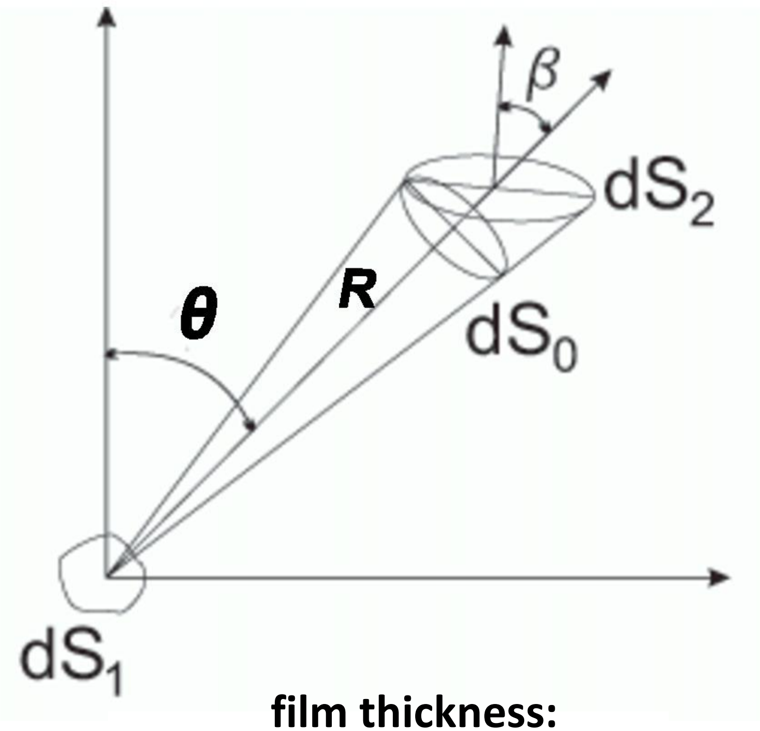


«boat» is fabricated from W, Ta, or Mo (very high melting temperatures)

$$\frac{dP_{sat}}{dT} = \frac{Q}{T\Delta V} \;\Rightarrow\; \frac{dP_{sat}}{dT} = \frac{PQ}{T^2 R} \;\Rightarrow\; \ln P_{sat} = -\frac{Q}{TR} + A = A - \frac{B}{T}$$

If PV~RT; Q – evaporation enthalpy

Thermal sputtering, distribution along the support surface

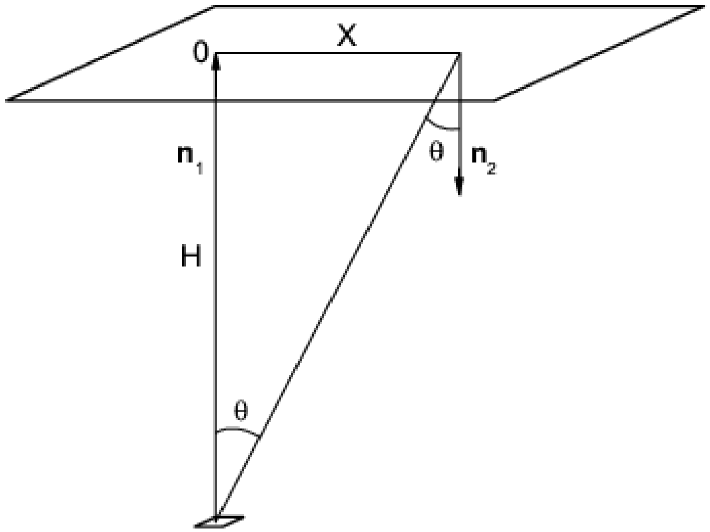


film thickness:

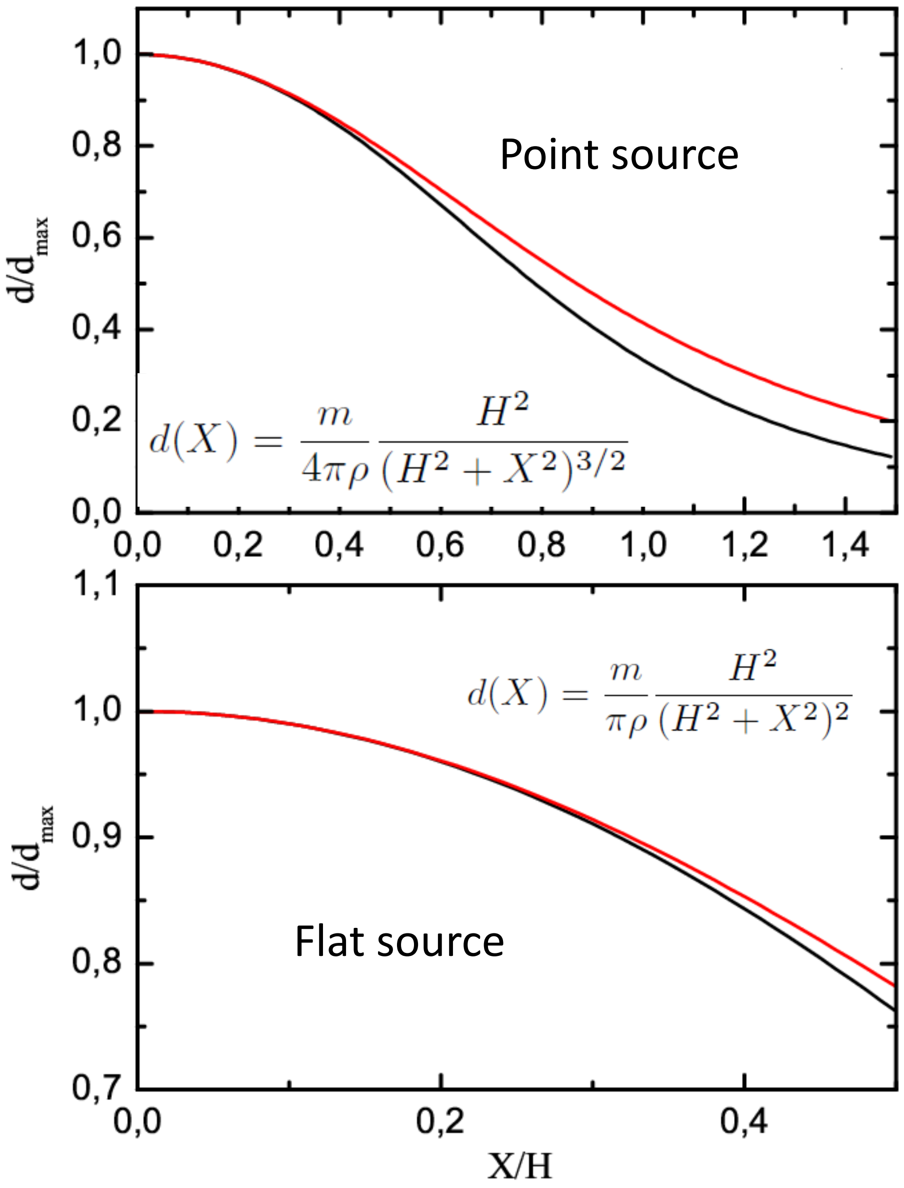
$$d = m\frac{\cos\theta\cos\beta}{\pi R^2\rho}$$ ⇦ density

for point source:

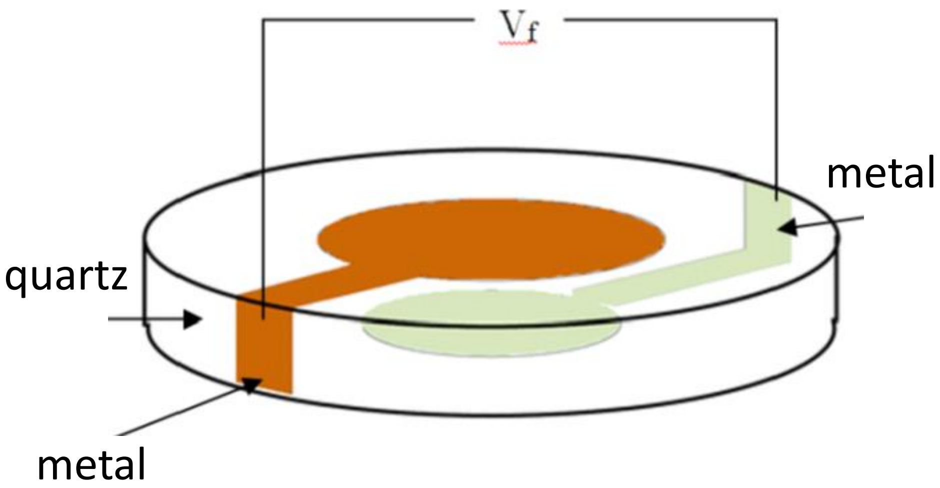
$$d = m\frac{\cos\beta}{4\pi R^2\rho}$$

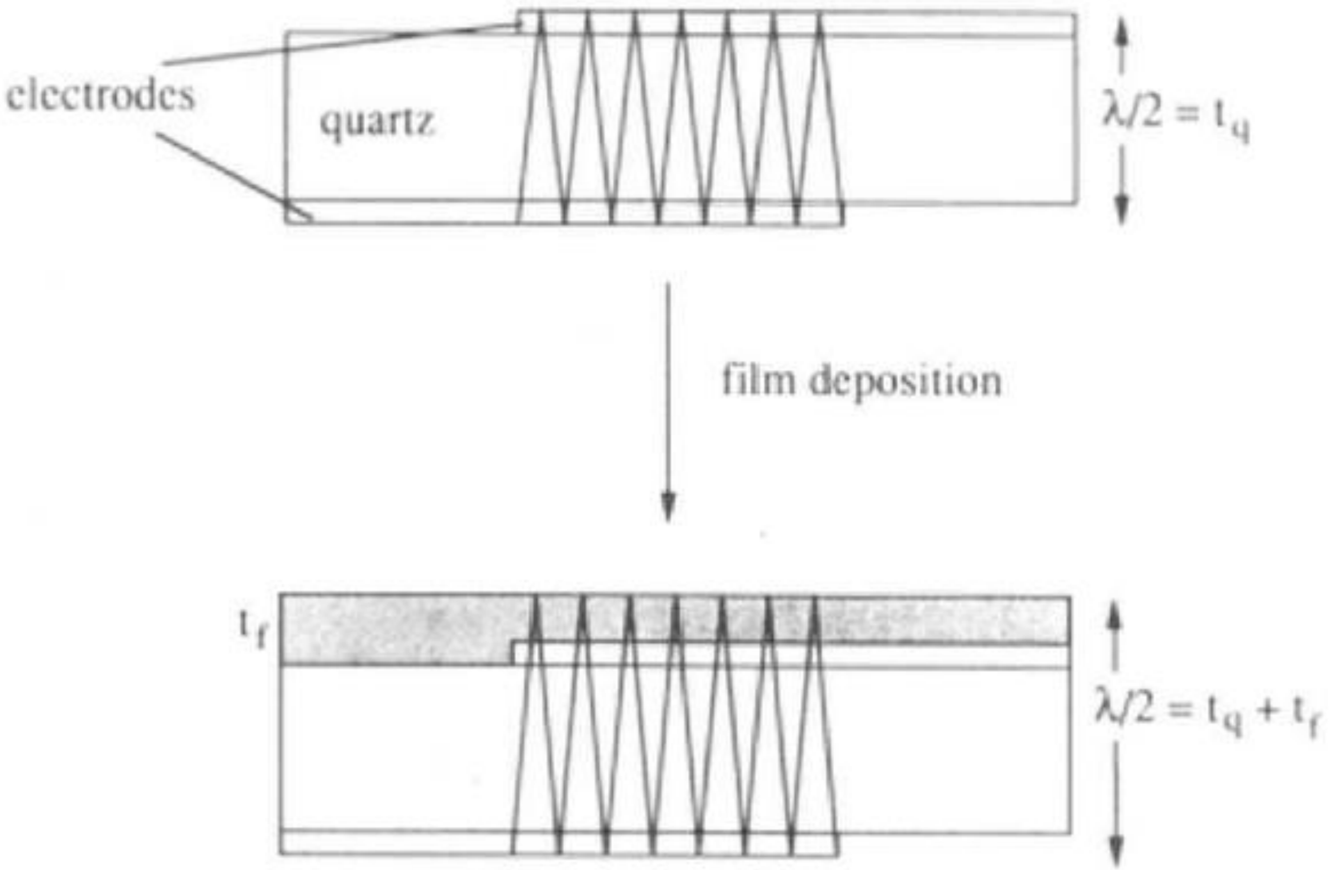


Example:
2x2 cm2 support
d accuracy 2.5%
H ~ 90 mm



Quartz crystal microbalance: monitoring of deposition rate





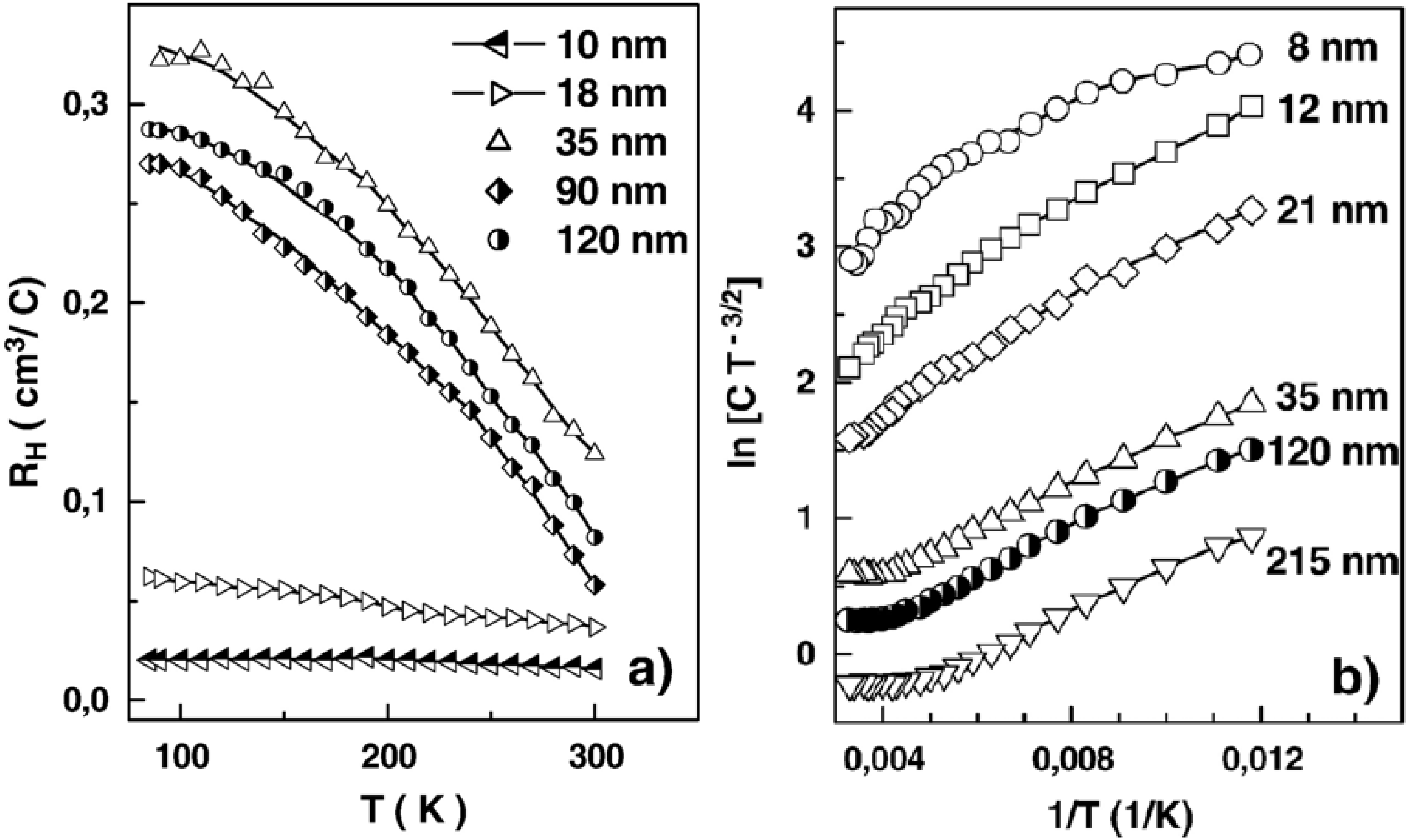
Sauerbrey equation:

$$\Delta f = -2{f_o}^2 \Delta m / A(\mu_q \rho_q)^{1/2}$$

- f_o: Quartz crystal resonant frequency
- A: Surface area
- ρ_q: Density
- Δf: Change of the resonant frequency
- Δm: Film mass
- μ_q: Shear modulus

The acoustic wavelength is longer after film deposition, due to the greater thickness, resulting in lower resonant frequency compared to bare quartz crystal.

Thermal sputtering, Bi on mica (111)

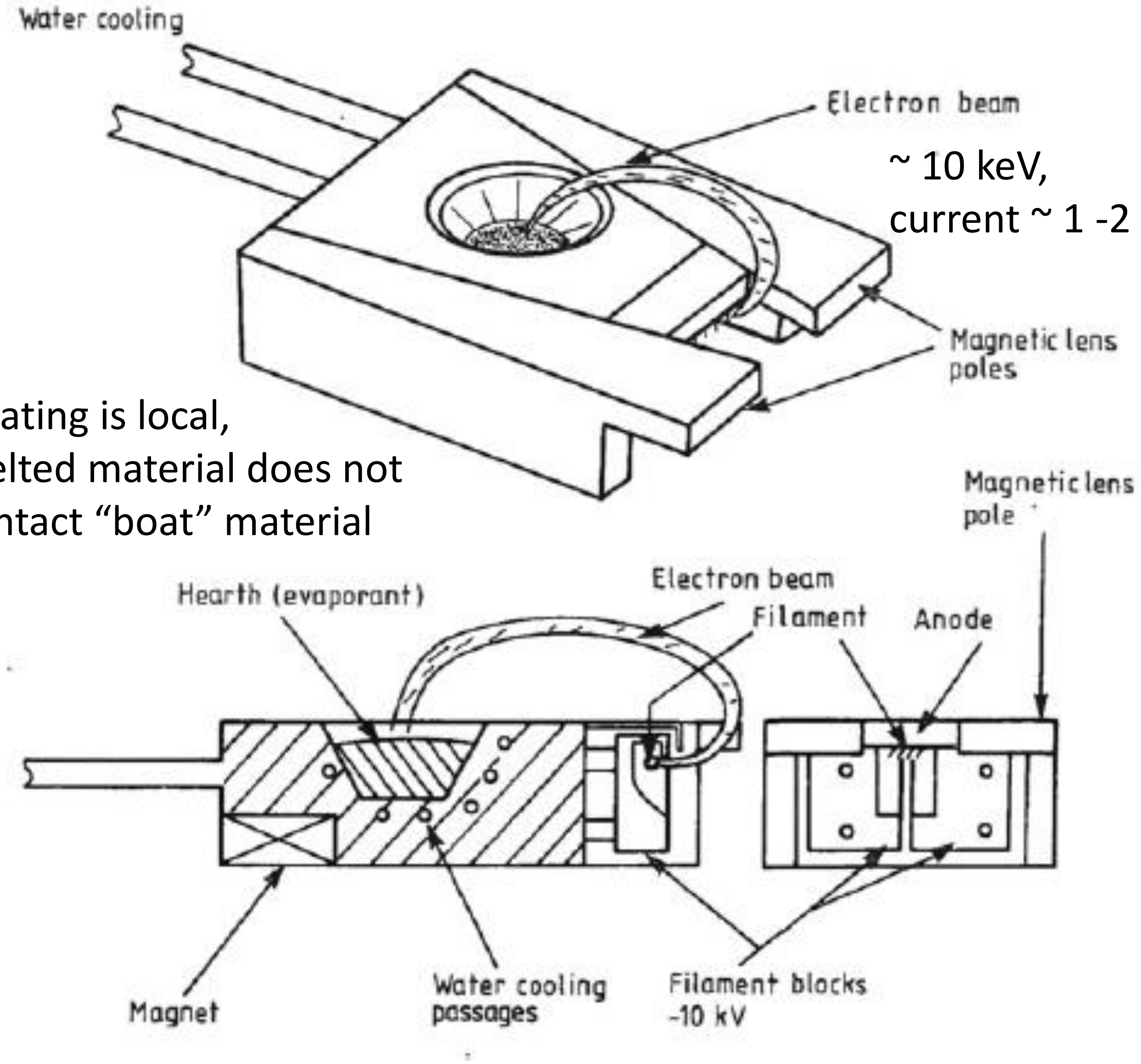


Compare with the data for Bi wires, Pts 1-2, p.13:

qualitative changes started from 45 nm wire diameter.

Thin Solid Films 516 (2008) 3411–3415

E-beam deposition



~ 10 keV,
current ~ 1 -2 A

Heating is local,
melted material does not
contact “boat” material

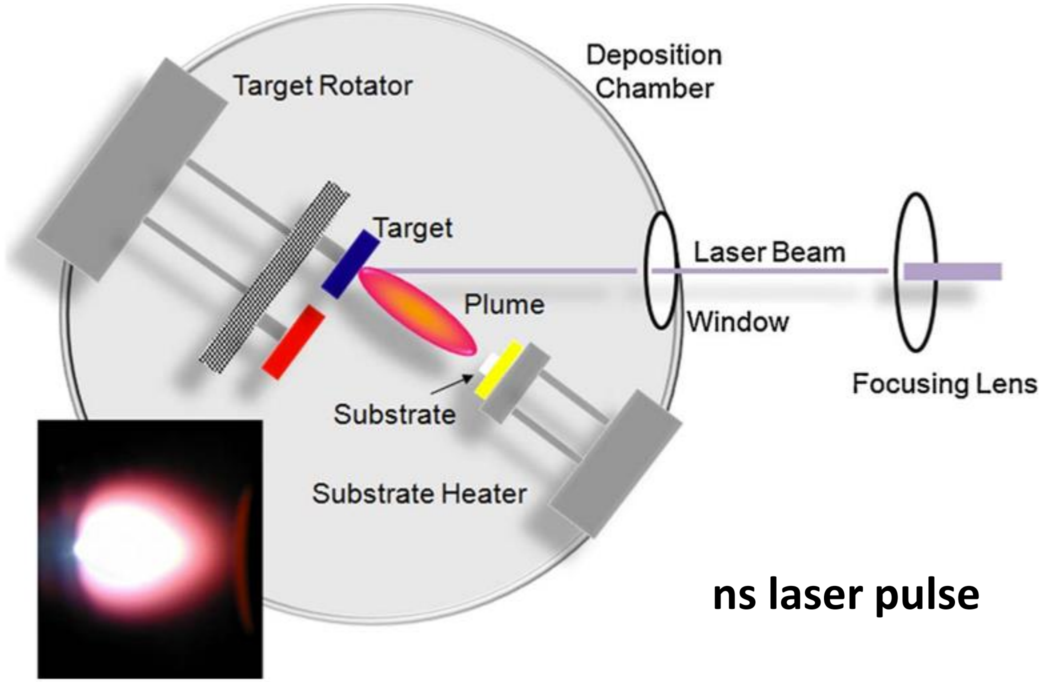
Plasma Sources Sci. Technol. 31 (2022) No 083001

Molecular beam epitaxy (MBE)

Vacuum < 10^{-12} bar

Diaphragms are applied to decrease the solid angle

Pulsed laser deposition (PLD)



Materials Sci. Eng. R 68 (2010) 89

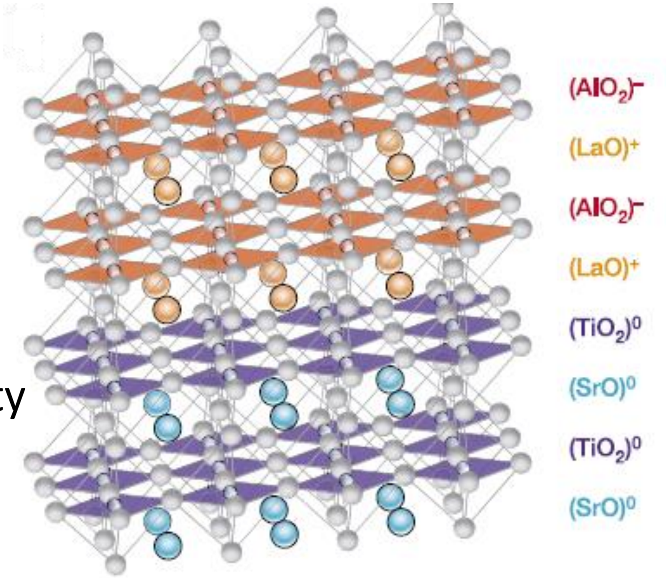
ns laser pulse

~ 10 nm layer is heated

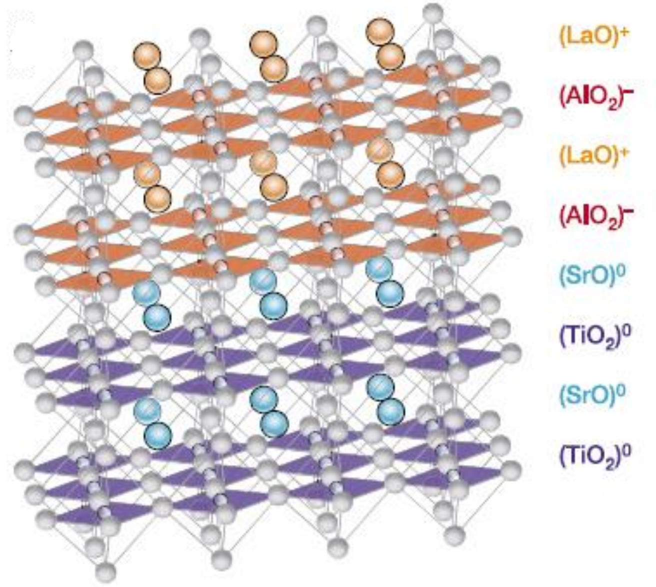
evaporation of clusters, not only atoms, is possible (laser ablation)

Deposition of $LaAlO_3$ on $SrTiO_3$

LaO-TiO2, n-type conductivity



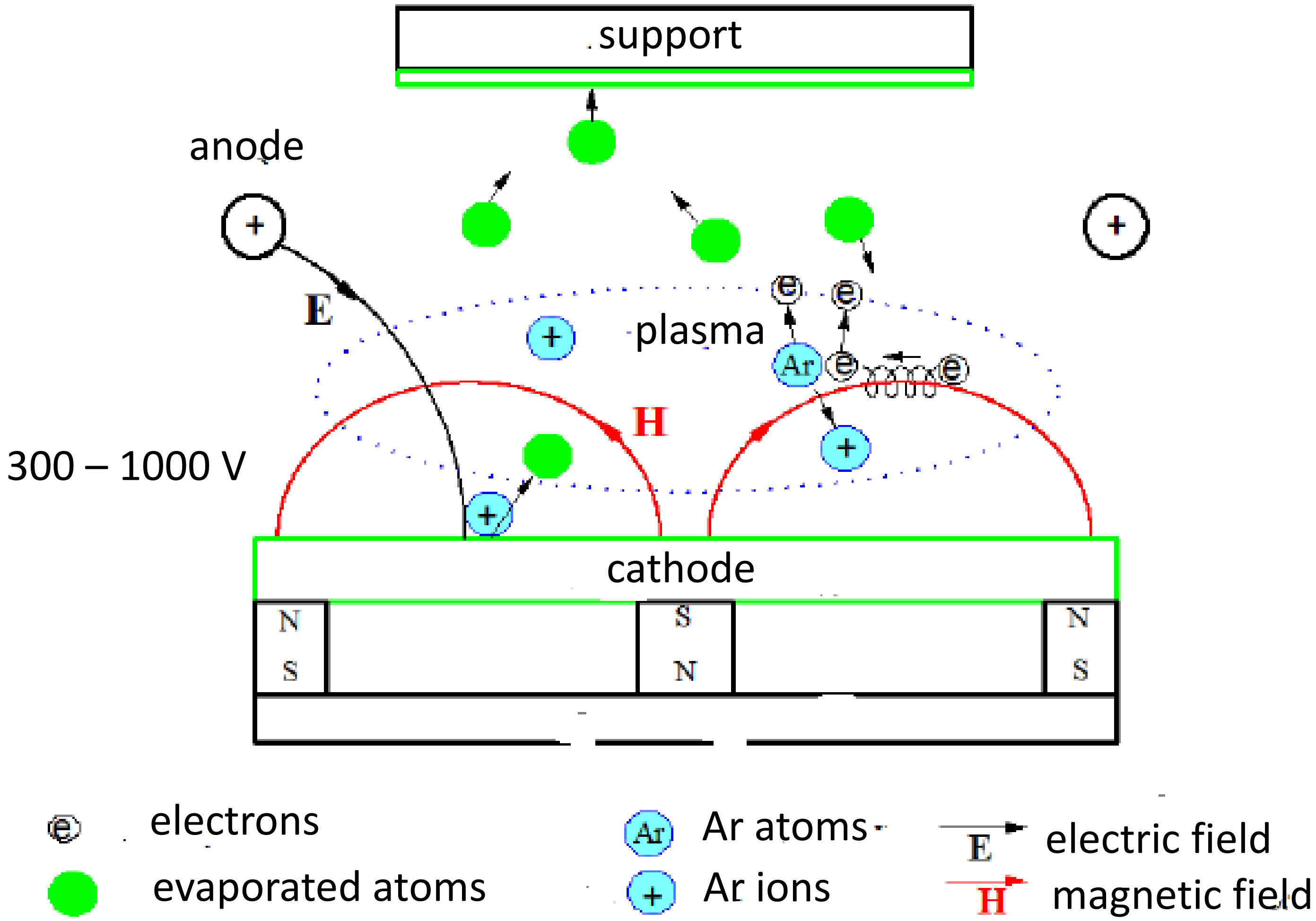
SrO-AlO2, insulating



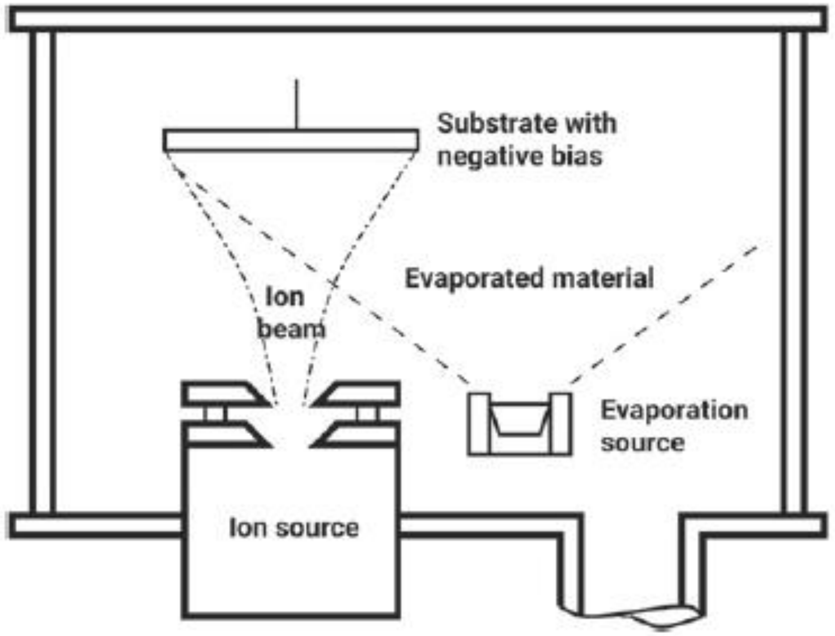
Nature 427 (2004) 423

Magnetron (plasma) sputtering

$10^{-6} - 10^{-3}$ bar Ar



Ion beam assisted deposition



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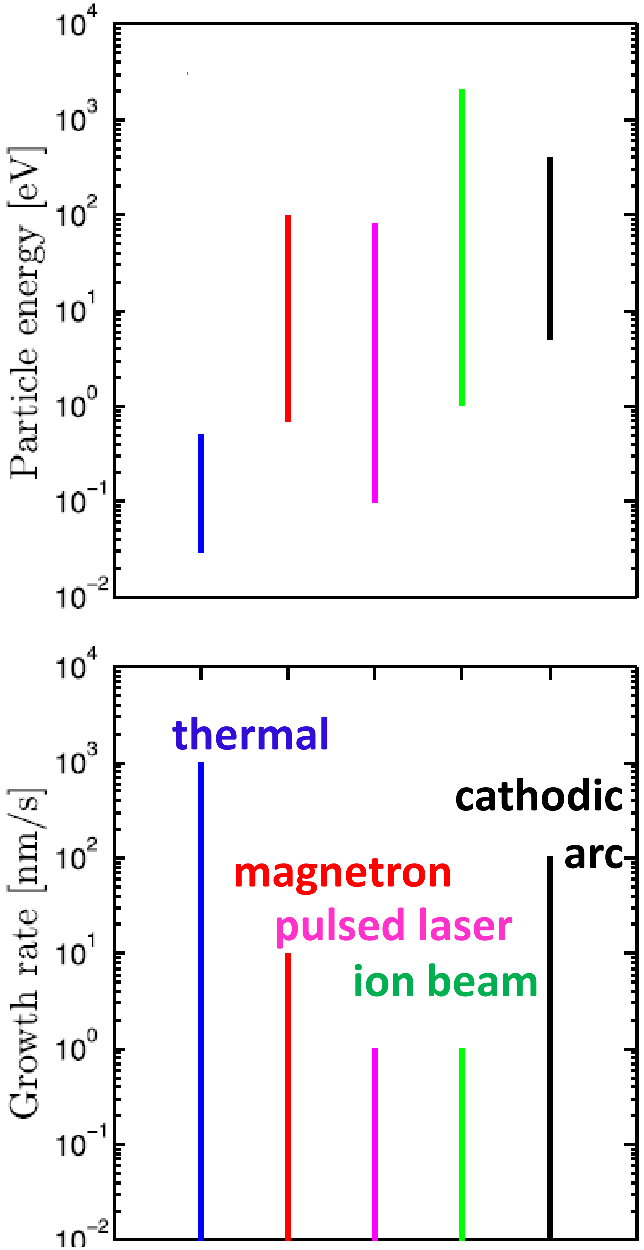
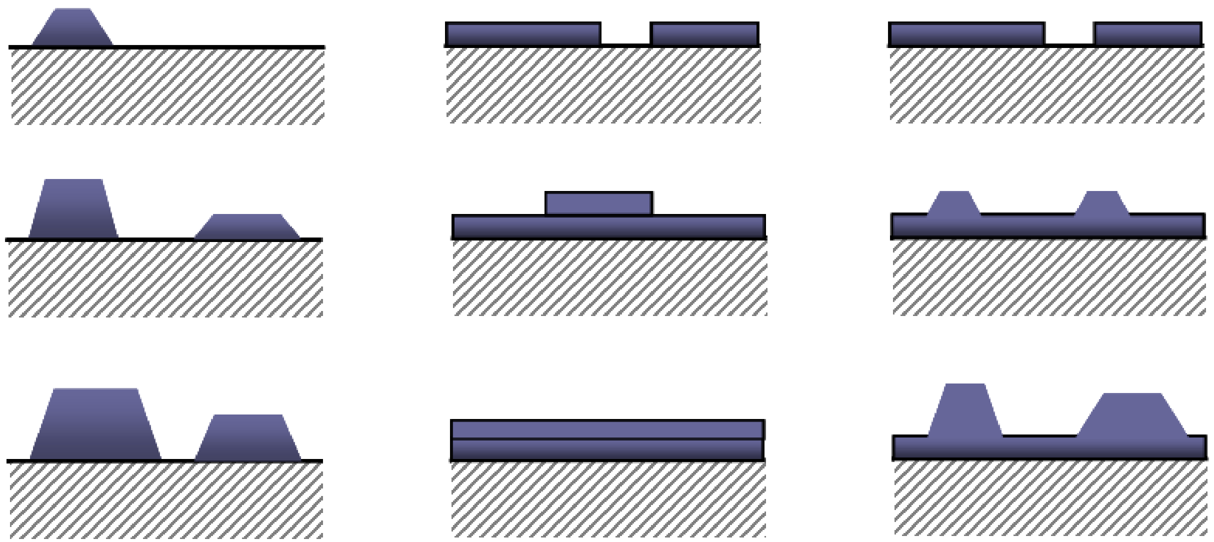
31 (2022) No 083001

Comparison of various physical vapor deposition techniques



Nucleation and growth:

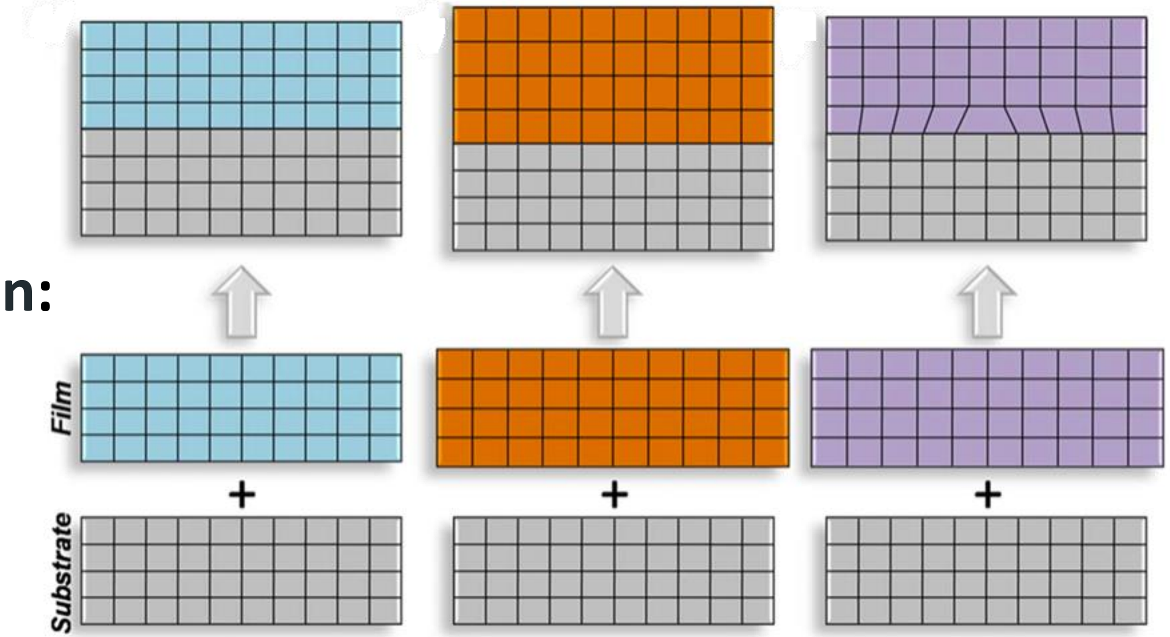


Island growth, Volmer–Weber

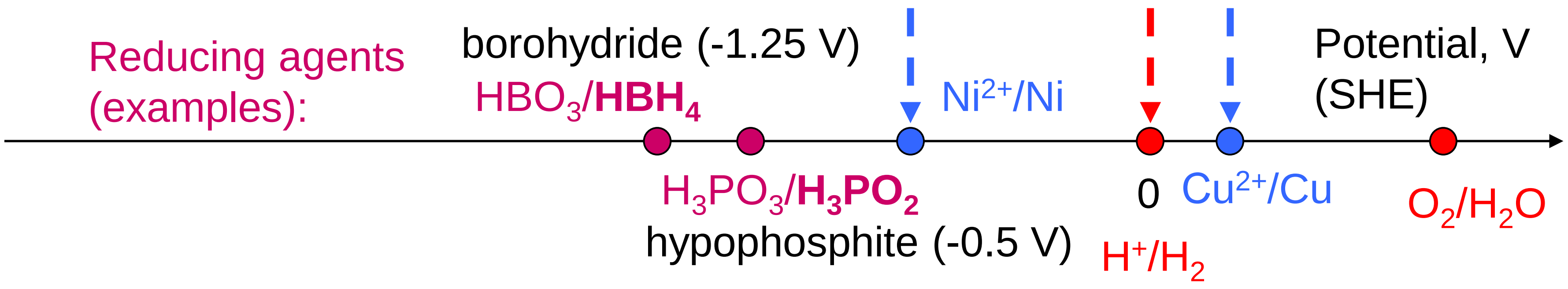
Layer-by-layer growth, Frank–VanderMerwe

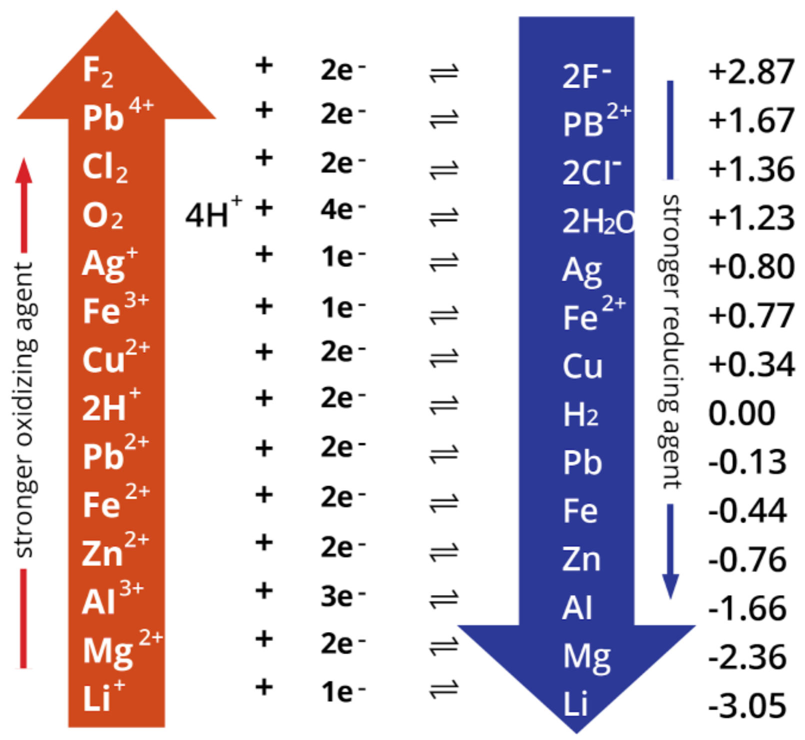
Islands on monolayer, Stranski–Krastanov

Lattice commensuration: (depends also on the temperature)



Wet deposition techniques: electroless (chemical) deposition (plating)





Half Reaction				Standard Potential (V)
F_2	+ 2e-	⇌	$2F^-$	+2.87
Pb^{4+}	+ 2e-	⇌	PB^{2+}	+1.67
Cl_2	+ 2e-	⇌	$2Cl^-$	+1.36
O_2	$4H^+$ + 4e-	⇌	$2H_2O$	+1.23
Ag^+	+ 1e-	⇌	Ag	+0.80
Fe^{3+}	+ 1e-	⇌	Fe^{2+}	+0.77
Cu^{2+}	+ 2e-	⇌	Cu	+0.34
$2H^+$	+ 2e-	⇌	H_2	0.00
Pb^{2+}	+ 2e-	⇌	Pb	-0.13
Fe^{2+}	+ 2e-	⇌	Fe	-0.44
Zn^{2+}	+ 2e-	⇌	Zn	-0.76
Al^{3+}	+ 3e-	⇌	Al	-1.66
Mg^{2+}	+ 2e-	⇌	Mg	-2.36
Li^+	+ 1e-	⇌	Li	-3.05

Electrochemical series (or Volta series); data of EMF measurements

ЭЛЕКТРОХИМИЧЕСКИЙ РЯД НАПРЯЖЕНИЙ МЕТАЛЛОВ

Li	Cs	K	Ba	Ca	Na	Mg	Al	Zn	Fe	Co	Ni	Sn	Pb	H_2	Cu	Ag	Hg	Pt	Au
-3,04	-3,01	-2,92	-2,90	-2,87	-2,71	-2,36	-1,66	-0,76	-0,44	-0,28	-0,25	-0,14	-0,13	0	+0,34	+0,80	+0,85	+1,28	+1,50
Li^+	Cs^+	K^+	Ba^{2+}	Ca^{2+}	Na^+	Mg^{2+}	Al^{3+}	Zn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Sn^{2+}	Pb^{2+}	2H	Cu^{2+}	Ag^+	Hg^{2+}	Pt^{2+}	Au^{3+}

Восстановительная активность металлов (свойство отдавать электроны) уменьшается, а окислительная способность их катионов (свойство присоединять электроны) увеличивается в указанном ряду слева направо.

$$d\overline{G} = \cancel{-SdT} + \cancel{Vdp} + \sum_i \mu_i dN_i + F\sum_i z_i \varphi dN_i$$

Electrochemical free energy

At constant temperature and pressure, under equilibrium:

$$\Delta_{solution}^{metal}\varphi = \varphi^{metal} - \varphi^{solution} = \frac{\mu^{solution} - \mu^{metal}}{zF}$$

Electroless deposition, reactions

copper

Reducing agent, dimethylamine borane

J. Mater. Chem. 14 (2004) 976

$$(CH_3)_2NHBH_3 + 2H_2O = BO_2^- + (CH_3)_2NH + 7H^+ + 6e^-$$

oxidation

target reactions

Reagent, citrate complex of copper

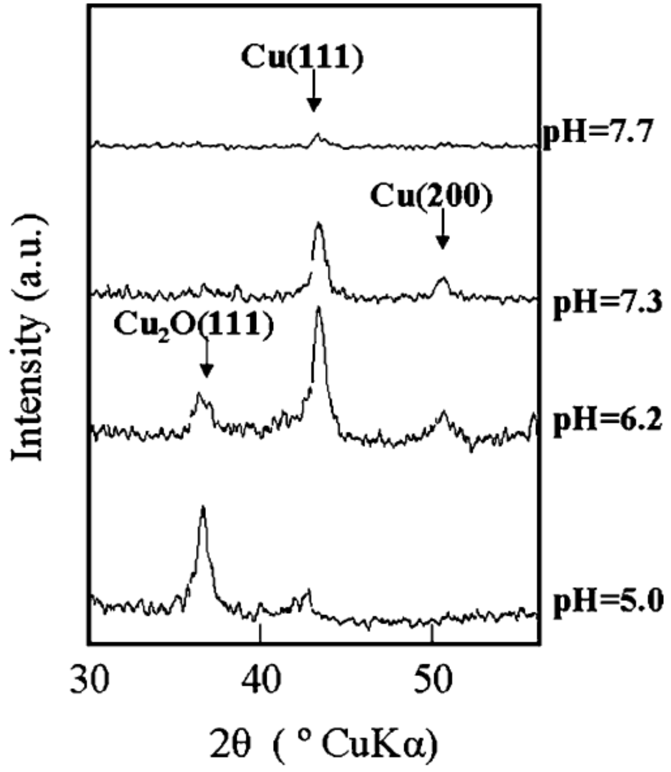
$$[Cu(C_6H_5O_7)]^- + 2e^- = Cu + C_6H_5O_7^{3-}$$

reduction

$$2[Cu(C_6H_5O_7)]^- + 2e^- + 2OH^- = Cu_2O + 2C_6H_5O_7^{3-} + H_2O$$

By-side reaction

By-side product (oxide)



Reaction rate depends on **concentrations** and on reaction free energy (**difference of equilibrium potentials** for half-reactions)

gold

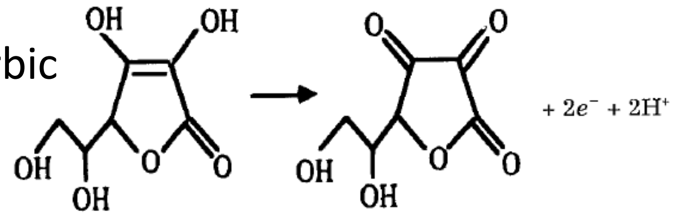
Initial deposition rates of electroless baths at pH 6.4, 30°C.

Reducing agent	[Reducing agent] (mol/l)	[Gold thiosulfate] (mol/l)	Initial deposition rates (μm/h) (±2σ)
Hydrazine	0.05	0.05	0.19 ± 0.04
Hydroxylamine	0.05	0.05	0.14 ± 0.04
Hypophosphite	0.05	0.05	0 ± 0.04
Ascorbic acid	0.05	0.05	1.26 ± 0.24
Ascorbic acid	0.05	0.03	0.89 ± 0.10
Ascorbic acid	0.05	0.01	0.69 ± 0.15
Ascorbic acid	0.03	0.05	0.54 ± 0.24

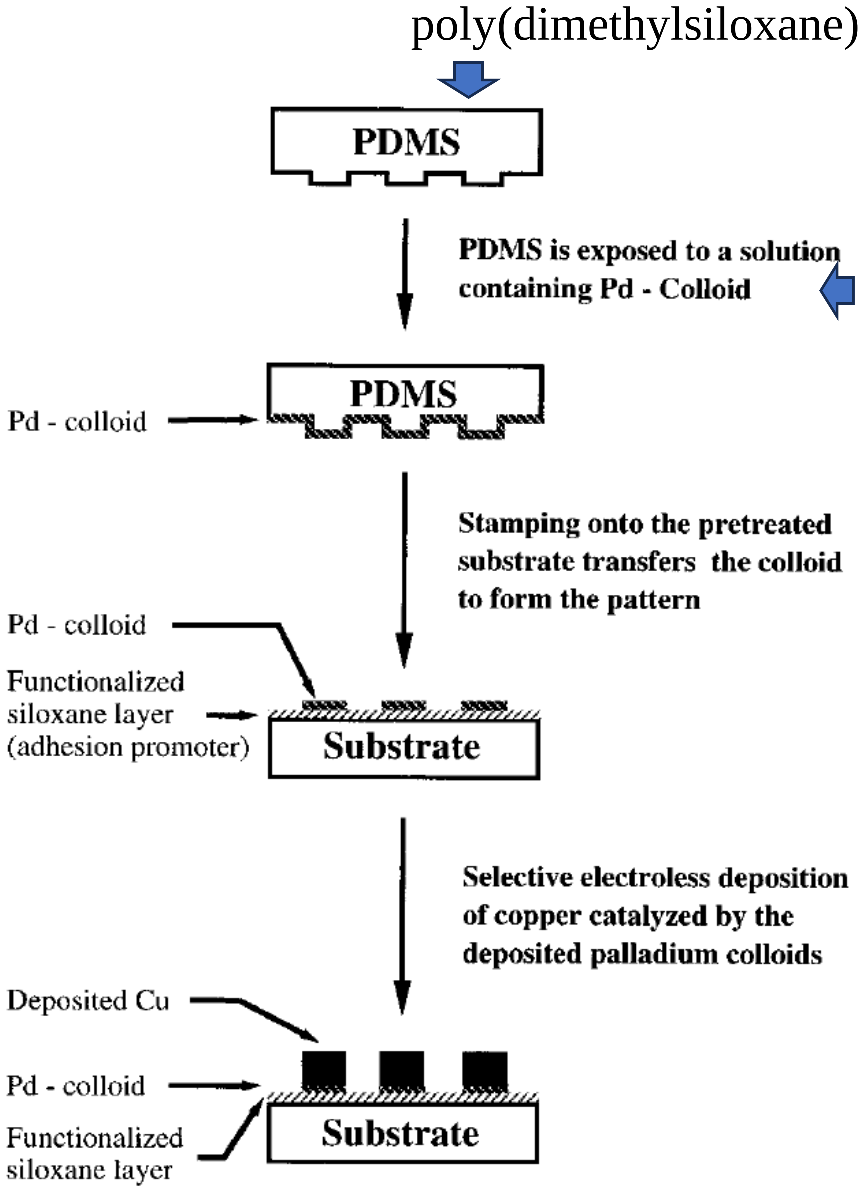
J. Electrochem. Soc. 142 (1995) 2250

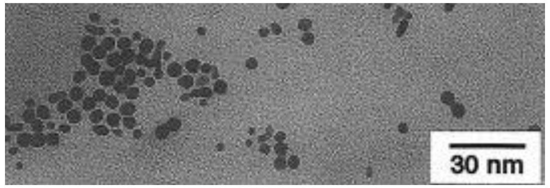
Hydrazine N_2H_4
Hydroxylamine NH_2OH
Hypophosphite $(PO_2)^{3-}$

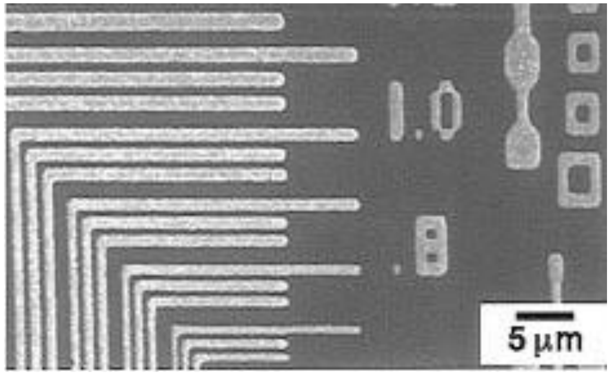
Ascorbic acid:

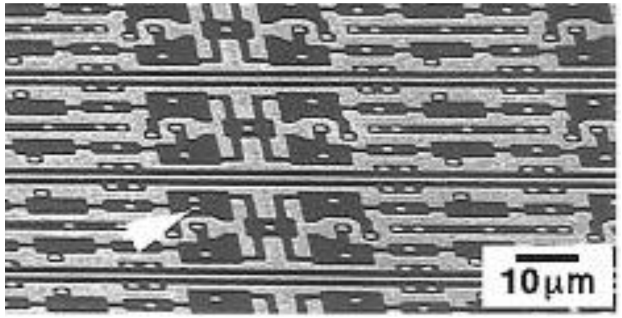


Electroless deposition: sensibilization of glass, polymers, and other hydrophobic surfaces





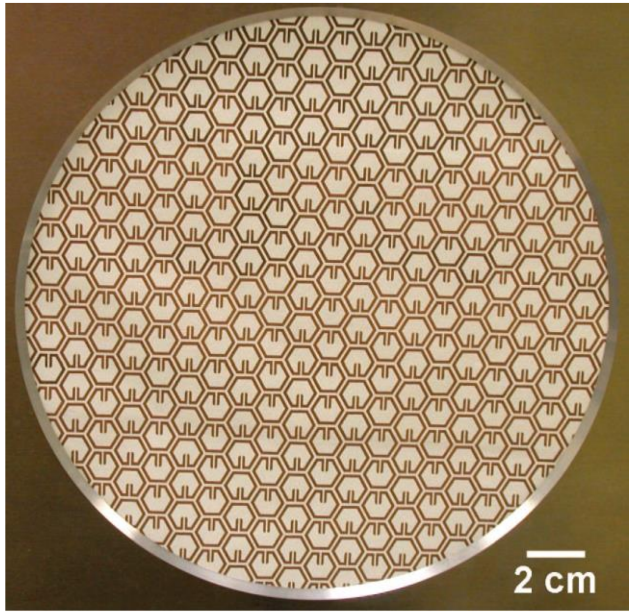




Langmuir 12 (1996) 1375

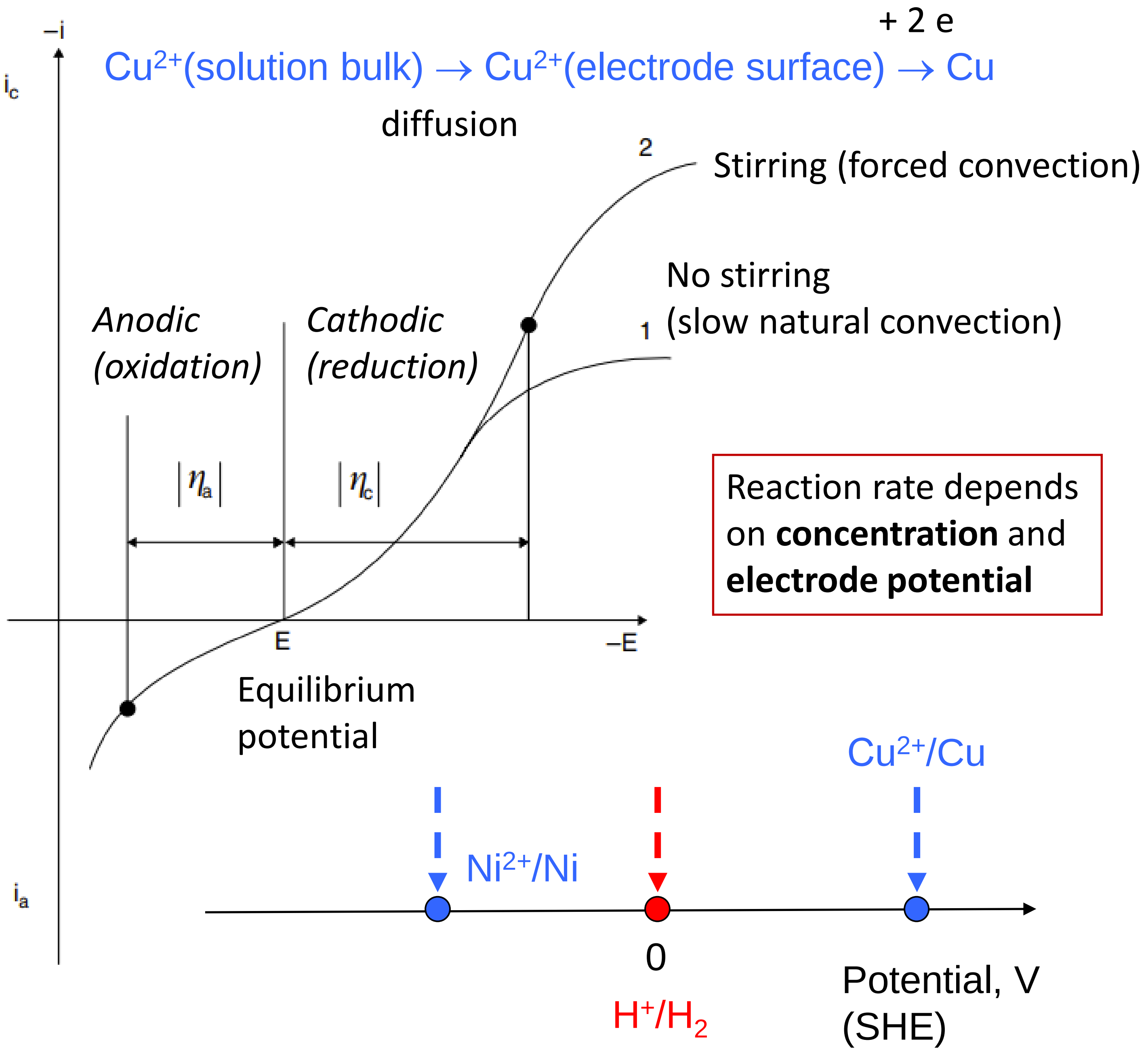
Typical sensibilization agents are tin, palladium and gold.

Cu resonators on paper



ACS Appl. Mater. Interfaces 1 (2009) 4

Wet deposition techniques: electrochemical (galvanic) deposition



Reaction rate depends on **concentration** and **electrode potential**

Electrolytes (bath) are designed for many metals to suppress hydrogen evolution

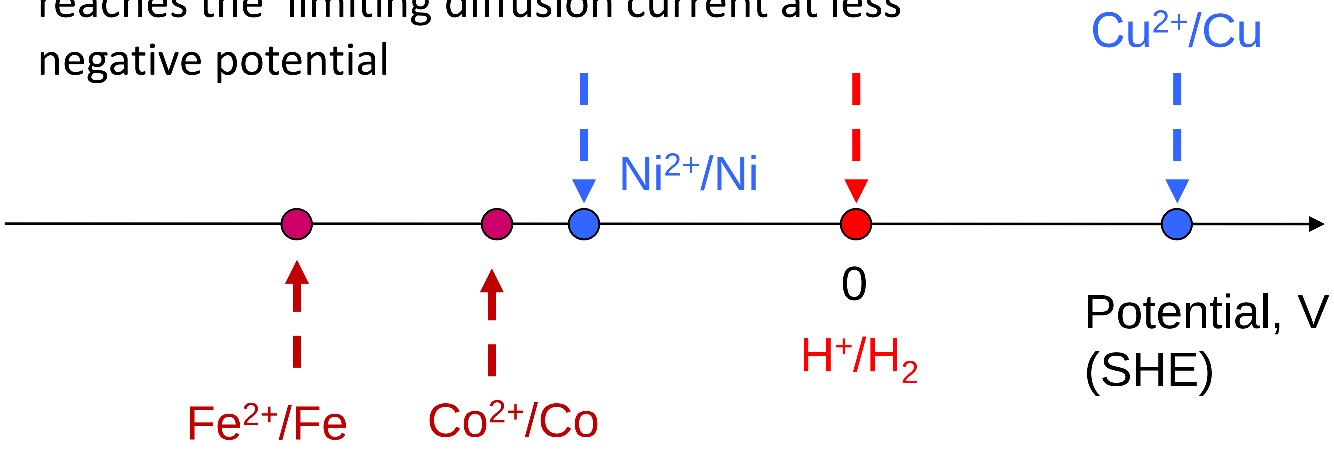
Metal	Type of the electrolyte	Average cathodic efficiency
Ag	Cyanide	0.98
Au	Citrate	0.60
Au	Phosphate	0.95
Cd	Cyanide	0.90
Cd	Sulf.-ammonia	0.90
Co	Sulfate	0.88
Cr	Chromate	0.18
Cu	Sulfate	1.00
Cu	Cyanide	0.75
Cu	Pyrohosphate	0.99
Fe	Chloride	0.90
Fe	Sulfate	0.92
Fe	Fluoroboric	0.95
Ni	Sulfate	0.96
Ni	Sulfamate	0.98
Pb	Fluoroboric	0.99
Pd	Amino-chloride	0.80
Re	Sulf.-ammonia	0.25
Rh	Sulfate	0.70
Sb	Citrate	0.94
Sn	Stannate	0.80
Sn	Pyrophosphate	0.90
Sn	Sulfate	0.95
Zn	Cyanide	0.80
Zn	Sulfate	0.97

Electrochemical deposition of alloys

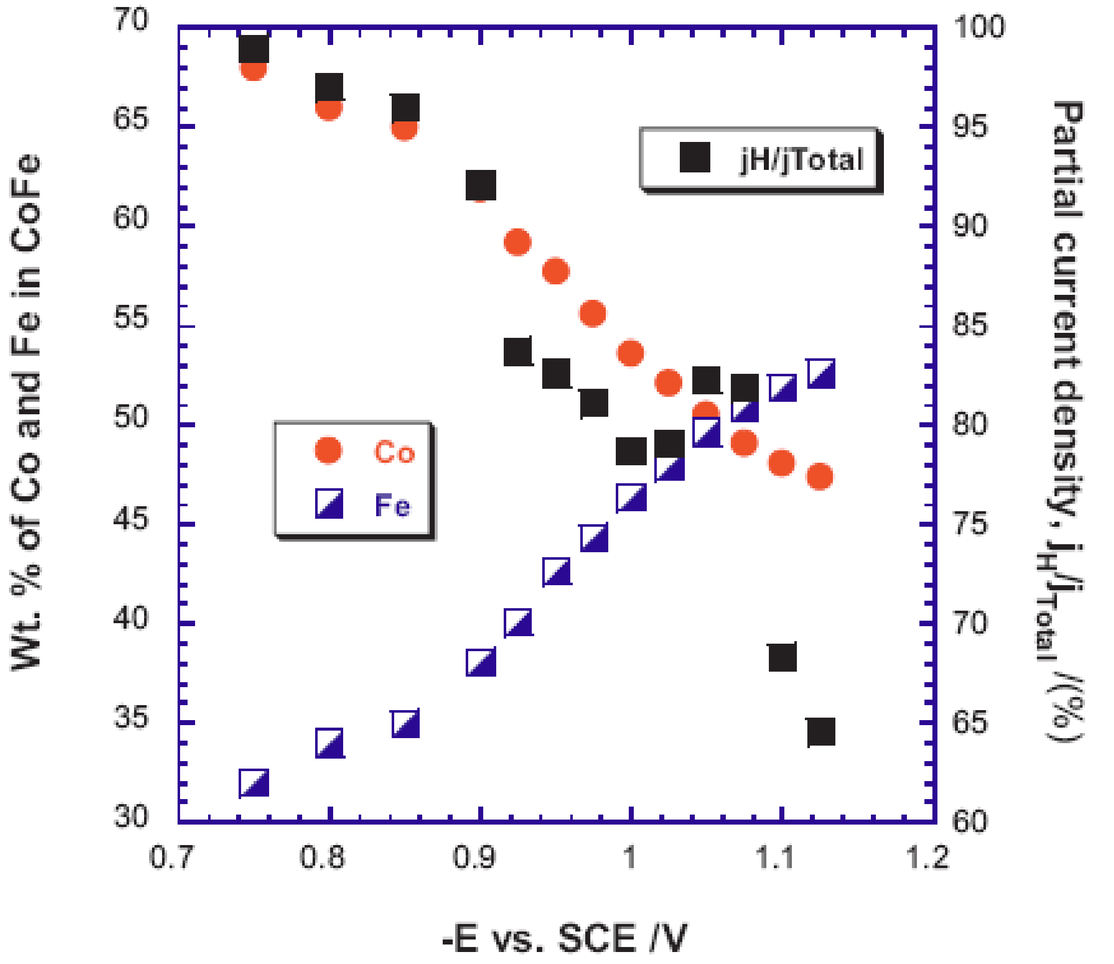
Composition of the plating solution.

Compound/condition	Value
NH_4Cl	0.3 M
H_3BO_3	0.4 M
Saccharin as Na-salt	0.004 M
$CoSO_4 \cdot 7H_2O$	0.05 M
$FeSO_4 \cdot 7H_2O$	0.0072–0.065 M
pH	2.3 ± 0.02
Temperature	23 ± 0.5 °C

More ‘noble’ metal is depositing faster, but reaches the limiting diffusion current at less negative potential

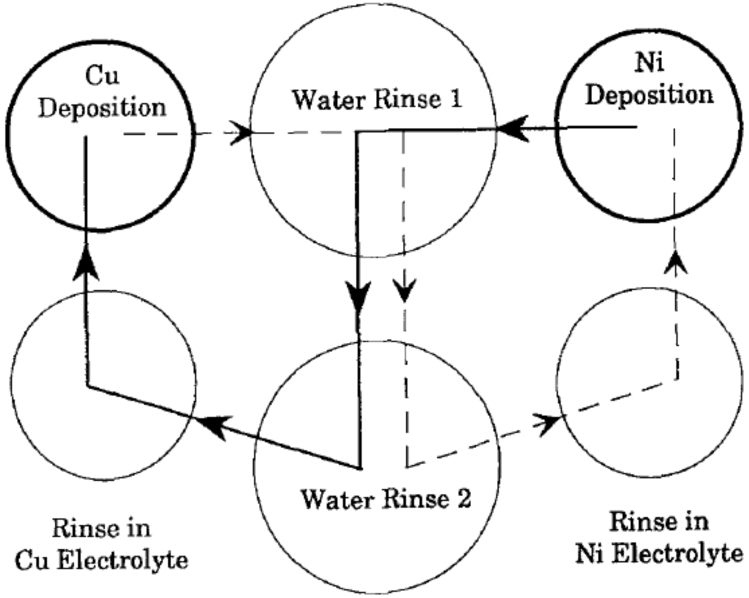


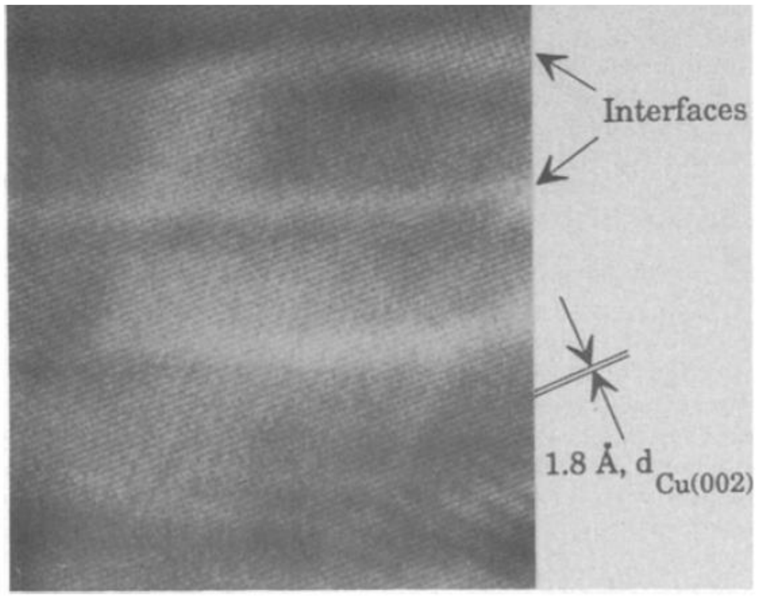
Parallel process: hydrogen evolution

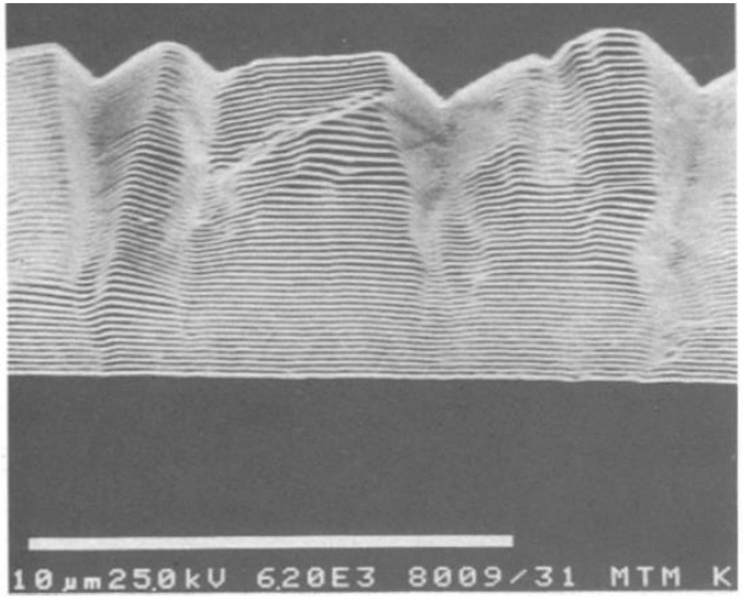


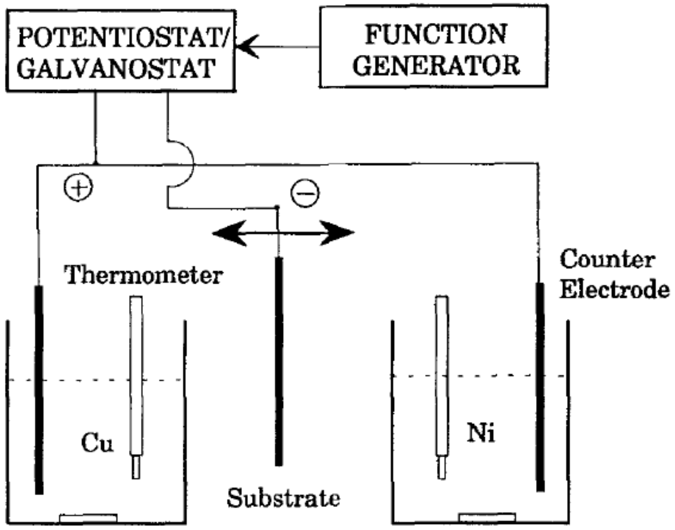
Electrochimica Acta 58 (2011) 25

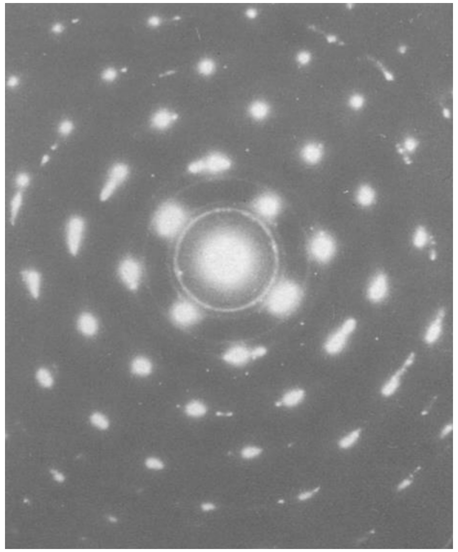
Electrochemical deposition of bimetallic superlattices: dual bath

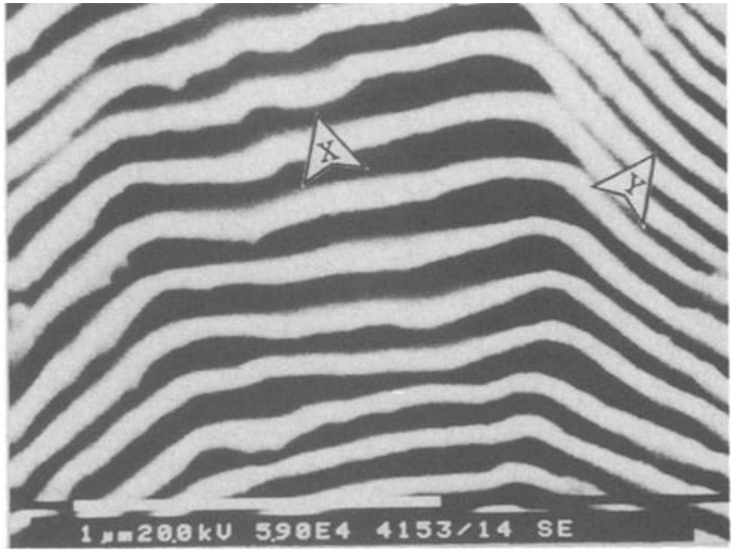






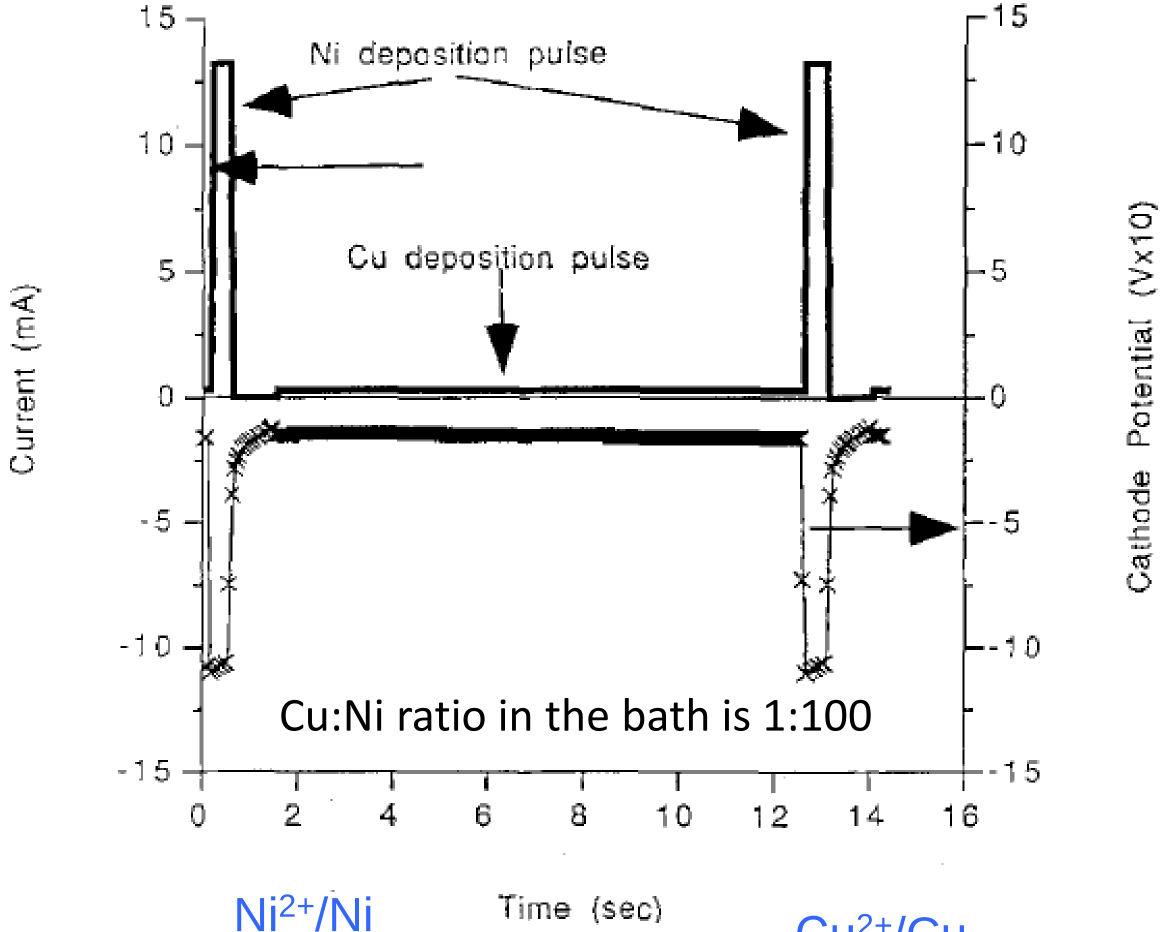


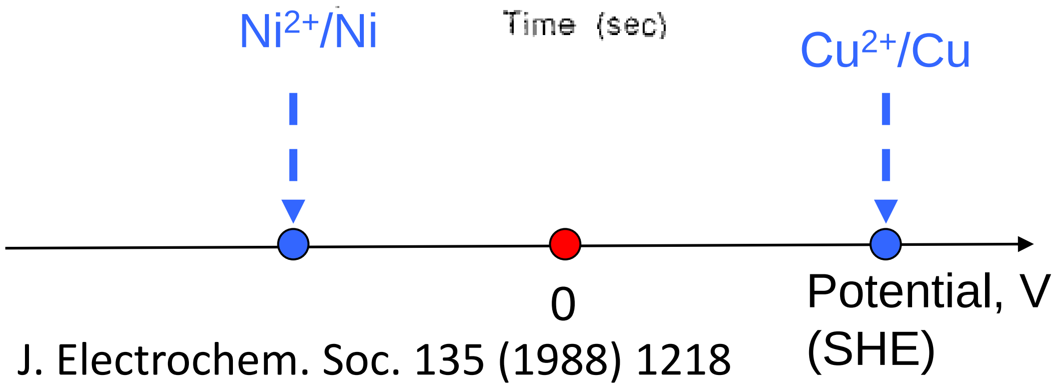




J. Electrochem. Soc. 141 (1994) 230

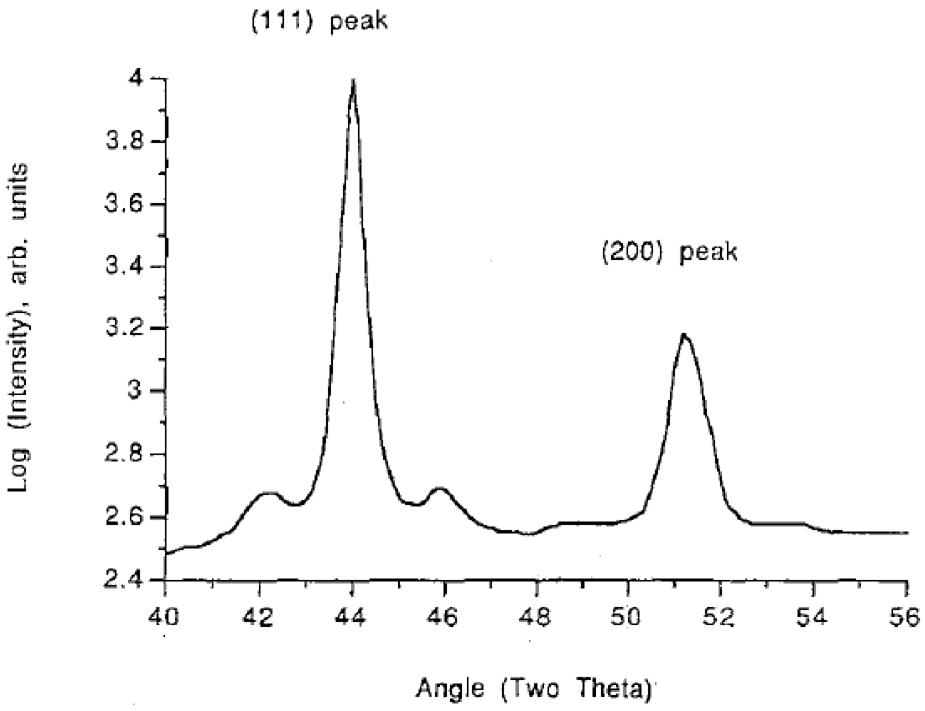
Electrochemical deposition of bimetallic superlattices: single bath





J. Electrochem. Soc. 135 (1988) 1218

2-3 nm thick layers in Cu/NiCu/Cu/….
Total thickness is 15 μm.



Satellite reflections appear in XRD pattern, which indicate superlattice formation.

Electrochemical deposition of binary compounds

$2Tl^+ + 6OH^- - 4e = Tl_2O_3 + 3H_2O$

$Pb^{2+} + 4OH^- - 2e = PbO_2 + 2H_2O$

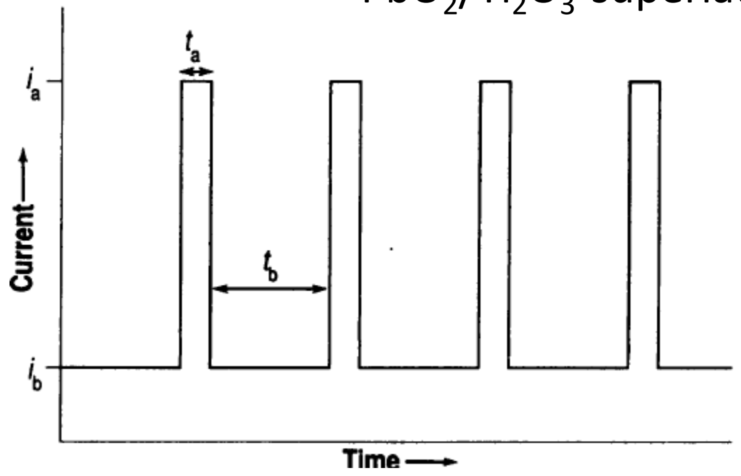
anodic deposition

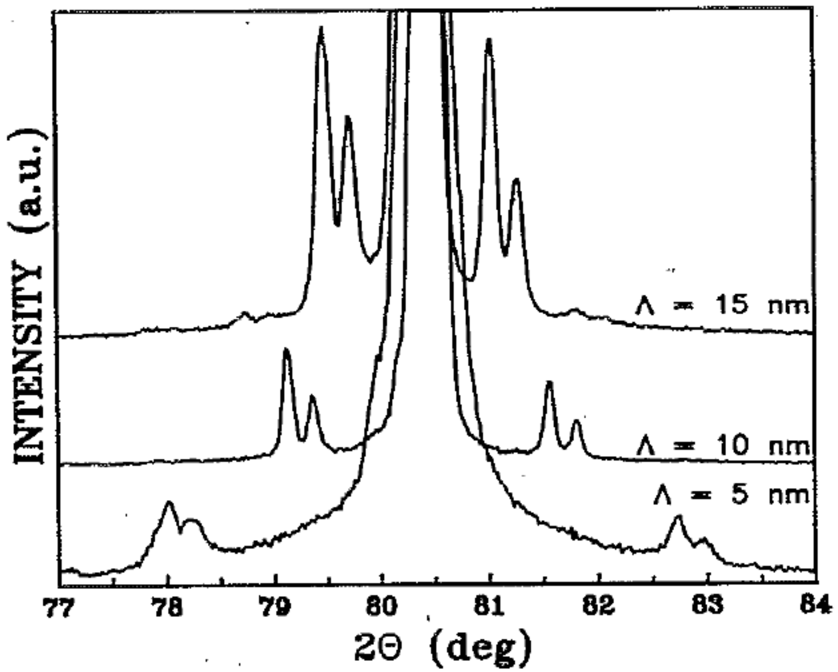
$2Cu^{2+} + 2OH^- + 2e = Cu_2O + H_2O$

$Cd^{2+} + (SeO_3)^{2-} + 3H_2O + 6e = CdSe + 6OH^-$

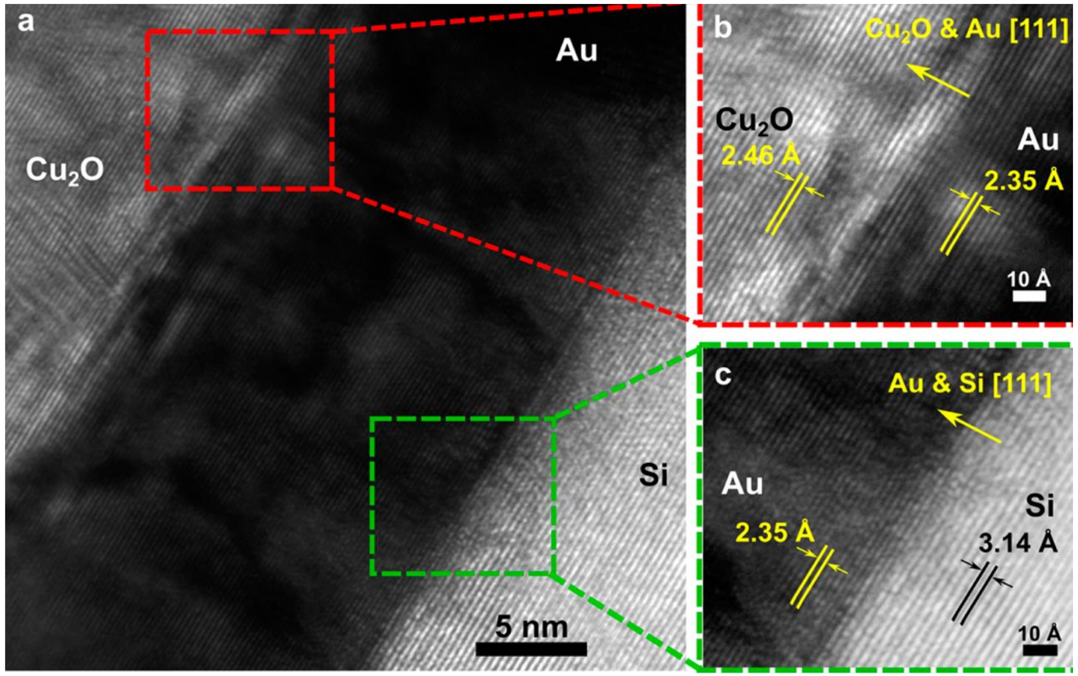
cathodic deposition

PbO_2/Tl_2O_3 superlattice



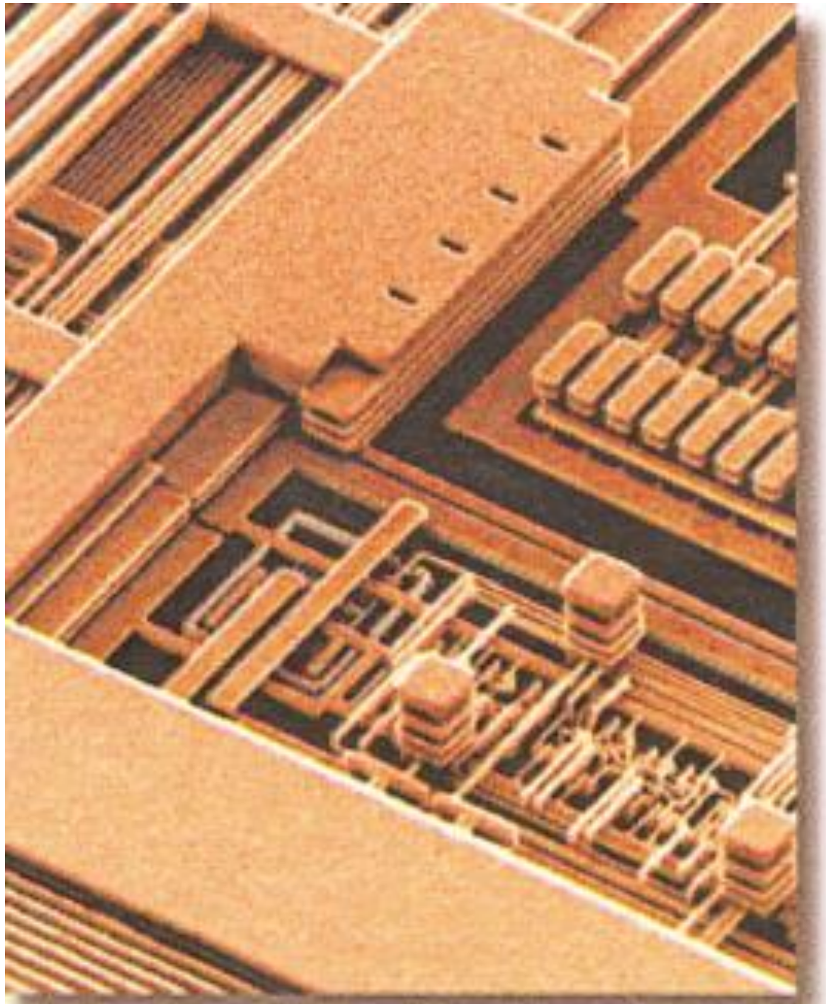


Science 247 (1990) 444
Appl. Phys. Lett. 63 (1993) 1501



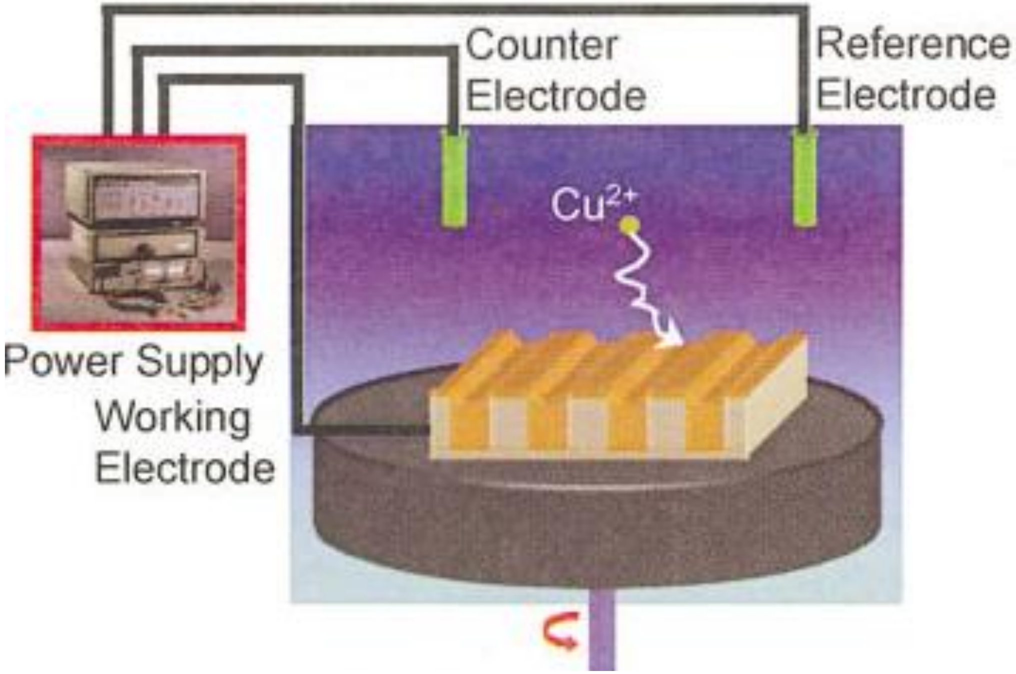
Cu_2O on Si epitaxial (Au sublayer)

ACS Appl. Mater. Interf. 8 (2016) 15828

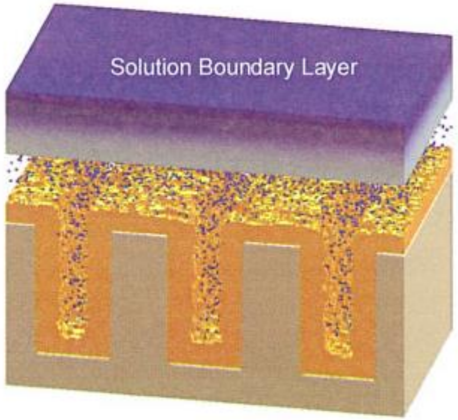


Multiple layers of electrodeposited copper wires (the non-copper materials have been etched away) that provide the on-chip 3-D network for interconnecting the transistors.

Copper interconnect technology was introduced by IBM in 1998, and is now widely used throughout the industry. Photo



Electrochemical process for manufacturing on-chip interconnects, in which a rotating disk creates a boundary layer above the wafer surface (not drawn to scale).



DAMASCENE process of copper deposition,

three additives:

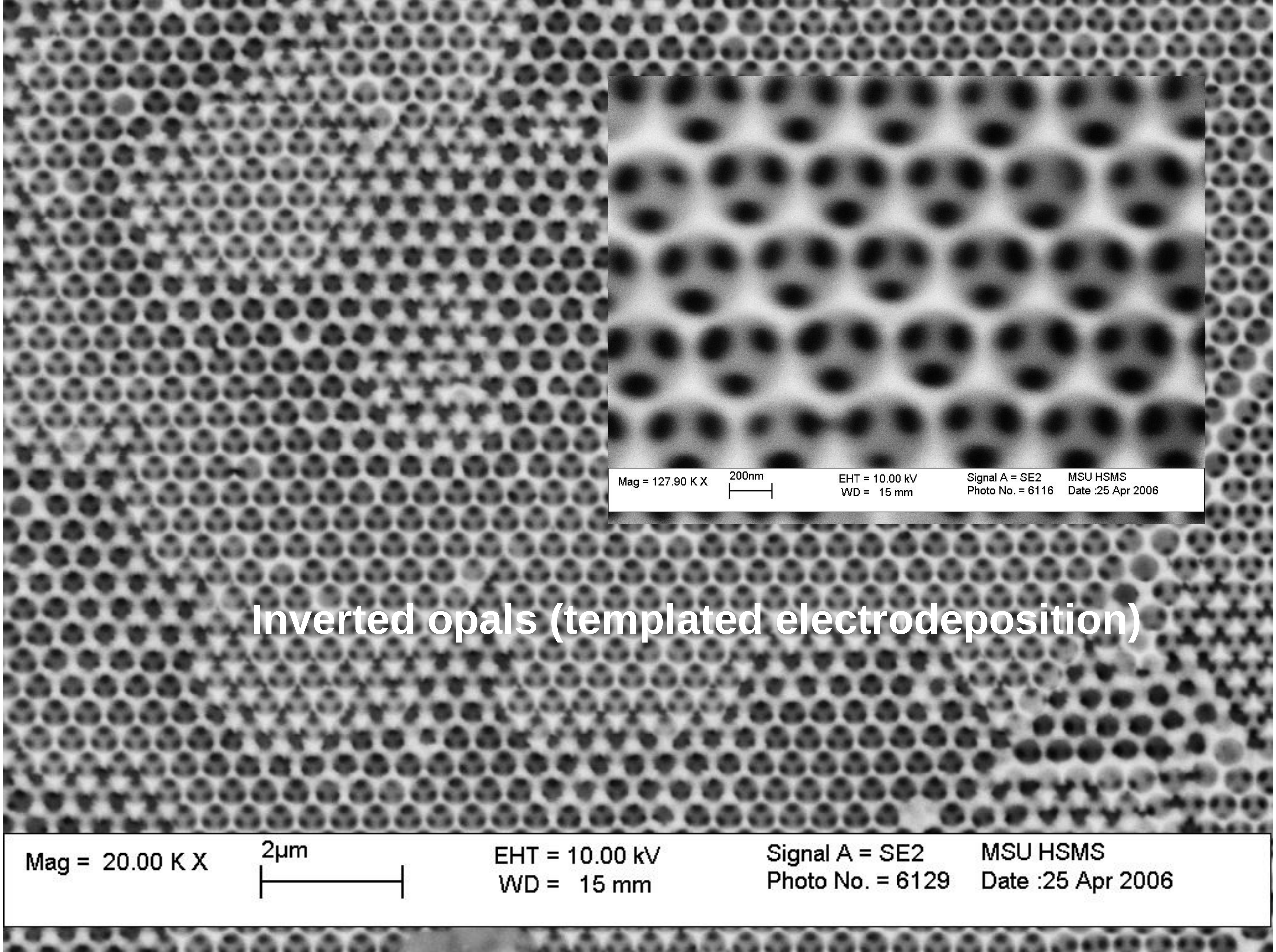
- ‘catalyst’

- suppressor

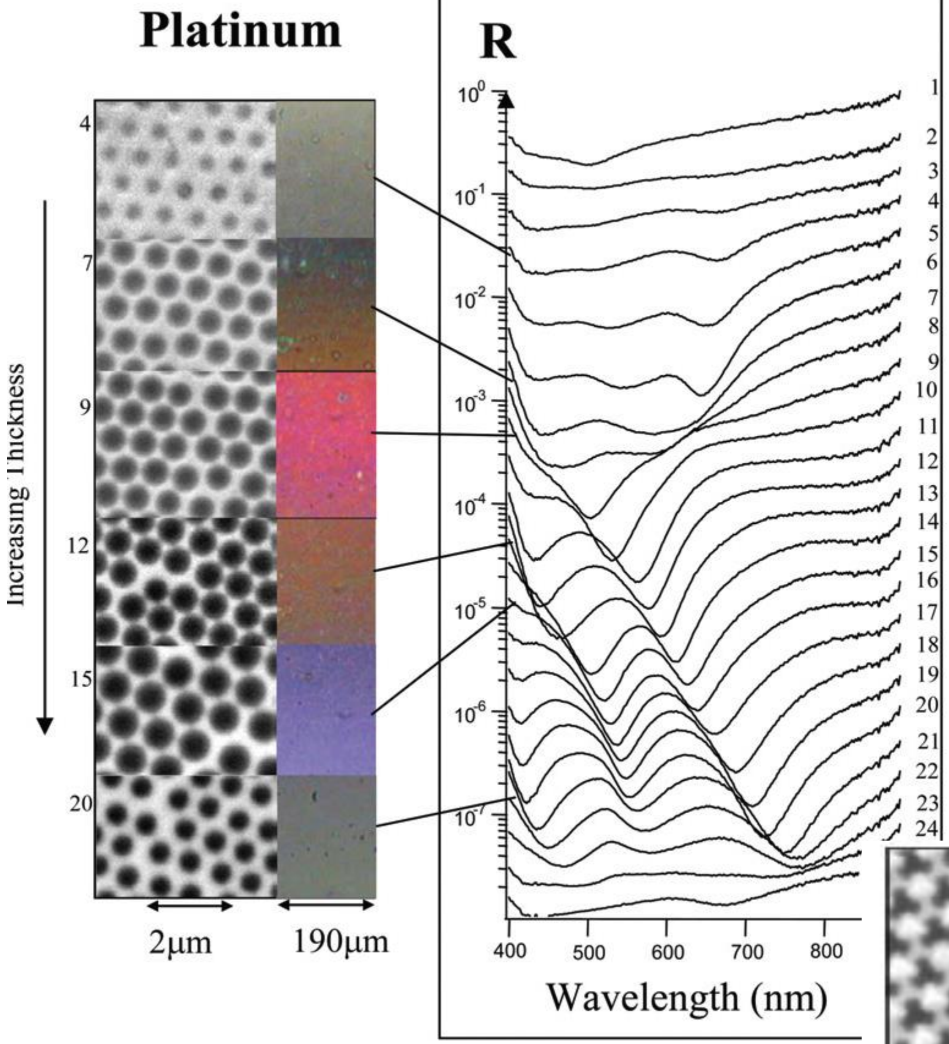
- ‘leveler’ (adsorbing species, also named ‘brighteners’)

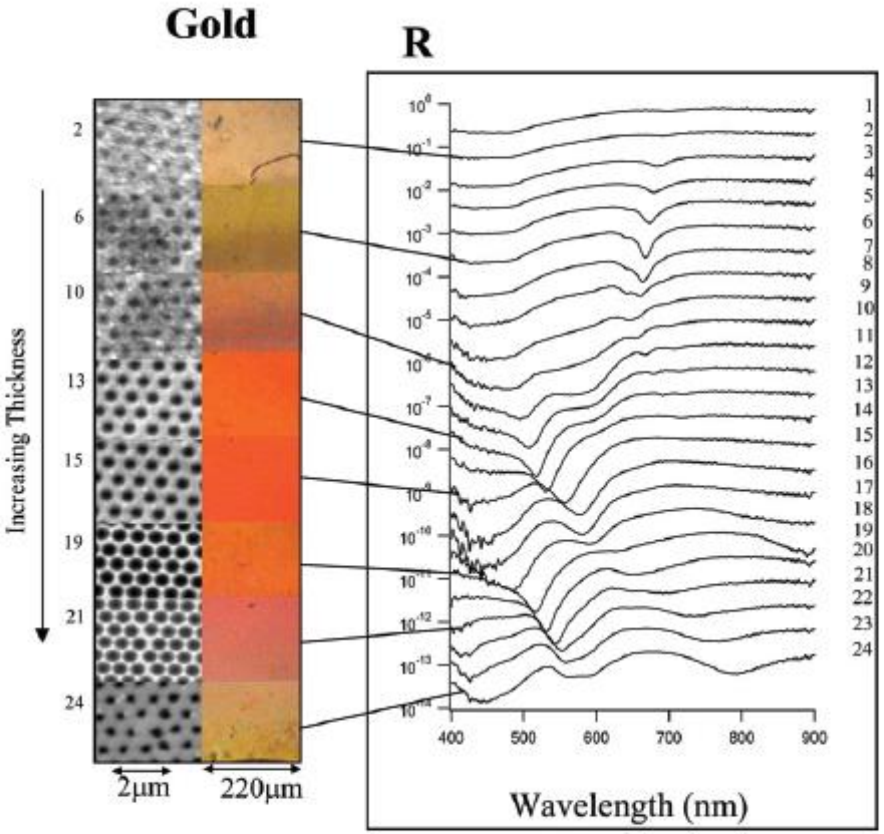
If diffusion of suppressor into narrow regions is slow, metal is in time to grow inside.

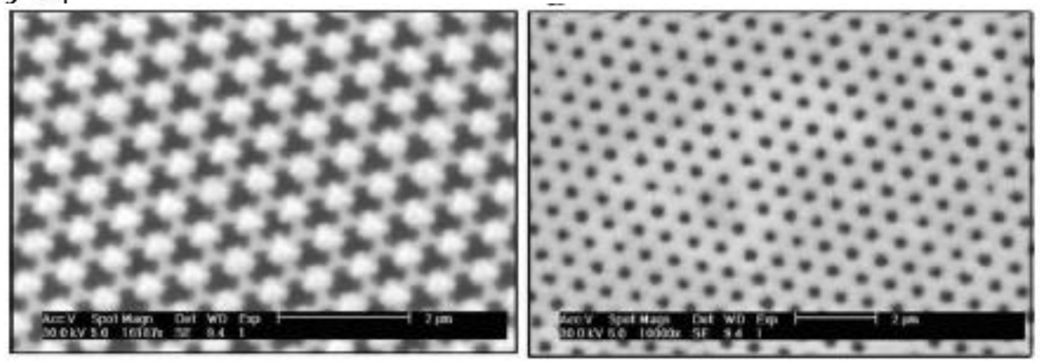
IBM Res. Devel. 49 (2005) No 1



Inverted opals (templated electrodeposition)







Faraday Discus. 125 (2004) 117

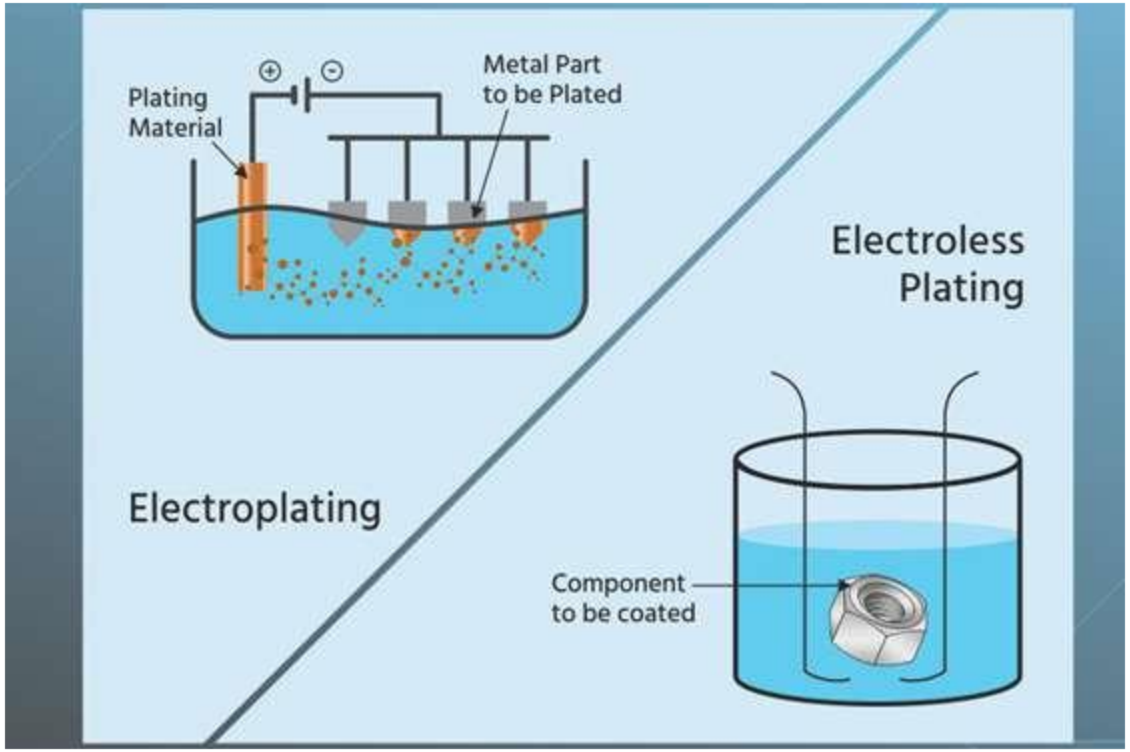
Electroless vs. electrochemical deposition (plating)

Electroless	Electrochemical
Any support	Only conducting supports
Simple configuration	Cell and contacts are necessary

Both are controlled by concentrations and temperature

Additional control by potential/current

Monitoring based on Faraday Law



Wet deposition vs. physical vapor deposition

Much lower temperatures

No contact with corrosive media

No damage by high-energy species

All real technologies combine wet and dry technological steps

Nanoelectronics

- spintronics
- cryoelectronics (*superconductor junctions and digital logics*)
- single electron devices (SETs)
- elements of organic electronics

Quantum computing

- superconductor qubits
- spin-based qubits
- electromagnetic traps for atoms and ions
- single electron qubits

Nanoelectronic emitters and detectors

- semiconductor light diodes
- single photon detectors (*semiconductor, superconductor*)
- emitters of electrons based on nm-size materials
- SQUID detectors
- SET-electrometers

Photonics and non-linear optics

- photonic crystals (*filters*)
- quantum micro resonators
- nanoplasmonics
- photonic integrated circuits
- single-photon sources

REMINDER

Tentative list of devices, which step-by-step technology we can discuss at the end of this course (Nov 24, 2023).

Please, send me your suggestions
galina.tsirlina@nanocenter.si
on or before Nov 9.

We shall vote for device the most interesting for the audience on Nov 10.

You can suggest something else as well,
in frames of nanotechnology definition.

2D material: books and reviews on sputtering and chemical/electrochemical deposition

- M. Paunovic, M. Schlesinger, Fundamentals of Electrochemical Deposition, Wiley, 2006.
- D. Zabetakis, W. J. Dressick, Selective Electroless Metallization of Patterned Polymeric Films for Lithography Applications, ACS Appl. Mater. Interfaces 1 (2009) 4-25.
- R.W. Martin, Y.-H. Chu, R. Ramesh, Advances in the growth and characterization of magnetic, ferroelectric, and multiferroic oxide thin films, Materials Sci. Eng. R 68 (2010) 89–133.
- M. Aliofkhazraei, A. S. Rouhaghdam, Fabrication of Nanostructures by Plasma Electrolysis, Wiley-VCH, 2010.
- Yu.D. Gamburg, G. Zangari, Theory and Practice of Metal Electrodeposition, Springer, 2011.
- M. Schlesinger, M. Paunovic, Modern electroplating, Wiley, 2011.
- Fundamentals of Electrochemical Deposition (editor U.S. Mohanty), Nova, 2012.
- Handbook of Sputter Deposition Technology (editors K. Wasa, I. Kanno, H. Kotera), Elsevier, 2012.
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- V. G. Dubrovskii, Nucleation Theory and Growth of Nanostructures, Berlin-Heidelberg, Springer, 2014.
- H. Frey, H.R. Khan, Handbook of Thin Film Technology, Springer, 2015.
- G. Greczynski, I. Petrov, J. E. Greene, L. Hultman, Paradigm shift in thin-film growth by magnetron sputtering: From gas-ion to metal-ion irradiation of the growing film, J. Vacuum Sci. Technol. A 37 (2019) No 060801.
- M. Powers, B. Derby, S.N. Manjunath et al., Hierarchical morphologies in co-sputter deposited thin films, Phys. Rev. Mater. 4 (2021) No 123801.
- J. Li, G.K. Ren, J.H. Chen et al., Facilitating Complex Thin Film Deposition by Using Magnetron Sputtering: A Review, JOM 74 (2022) 3069-3081.
- J.T. Gudmundsson, A. Anders, A. Keudell, Foundations of physical vapor deposition with plasma assistance, Plasma Sources Sci. Technol. 31 (2022) No 083001.