SEM sample preparation

REFRESHER COURSE: **CLEANING (DRY ETCHING – ION BEAM) AND COATING**

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SEM sample preparation

General characteristic for sample preparation:

- must be **conductive** to prevent charging
- must be **vacuum compatible**
- dependent on the **material properties**

Will ultimately determine image information

Figure removed for copyright reasons.

We will skip:

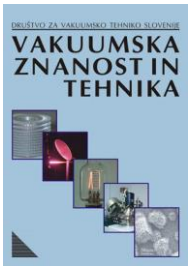
- basic steps for specimen preparation: cutting, mounting, grinding, polishing, cleaning*
- preparation of powders, bulk metals, semiconductors, …
- vacuum system, pumps, …

(Image: spectroscopynow)

Vacuum

The division of areas of low pressure:

abbreviation	Vacuum area	Pressure [mbar]	numerical density [particles/m^3]
LV (sl: GV)	low (rough) vacuum	1000 - 1	10^{19} - 10^{16}
MV (sl. SV)	medium vacuum	1 - 10^{-3}	10^{16} - 10^{13}
HV (sl. VV)	high vacuum	10^{-3} - 10^{-7}	10^{13} – 10^{9}
UHV (sl. UVV)	ultra high vacuum	10^{-7} - 10^{-12}	10^{9} - 10^{4}
EXV (sl. EVV)	extremely high vacuum	under 10^{-12}	under 10^{4}



Atmospheric pressure: 760 Torr = 101.3 kPa = 1013 mbar

760 Torr ≈ 1 bar → **Torr ~ mbar**
1 mbar = 100 Pa

Pressure: **Pa (SI unit)**, mbar, bar, Torr (USA)

Attaching the specimen

Carbon tape is spongy.

Figure removed for copyright reasons.

(Image: pdx)

Clean surface

- Avoid hydrocarbon contamination
- Low voltages
- Plasma cleaning
- Heating the sample
- Ion etching
- Environmental SEM – no alterations to the sample

(Image: Hitachi)

Etching process

Etching – the process by which material is removed from a surface

Wet etching - substrates are immersed in a reactive solution (etchant). The layer to be etched is removed by chemical reaction or by dissolution. The reaction products must be soluble and are carried away by the etchant solution.

(Image: Misumi)

(Image: TPC)

Etching process

Dry etching - substrates are immersed in a reactive gas (plasma). The layer to be etched is removed by chemical reactions and/or physical means - ion bombardment. The reaction products must be volatile and are carried away in the gas stream.

- Plasma etching: typically high pressure, no ion bombardment (substrate placed on grounded electrode).
- Reactive ion etching: typically lower pressures, ion bombardment (substrate placed on powered electrode)
- Ion beam methods: plasma is generated in a separate chamber and ions are accelerated towards the substrate (independently control flux of radicals and ions).
- Beam methods: plasma is generated in a separate chamber and mainly neutrals active species (radicals) are directed towards substrate.

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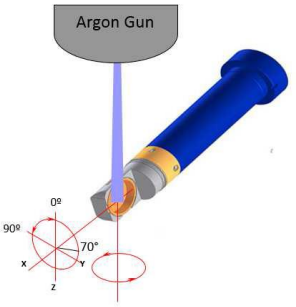
(Image: IOM)

Ion Etching - PECS

bench-top instrument

broad beam - 1 cm^2 area

Beam energy: 1 – 10 keV



For EBSD measurement:

- 60 ° -70° tilt
- best results obtained with low kV (2 kV - 3 kV)

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(Image: spectroscopynow)

Hints for etching

Table 4-1 Useful hints for etching specimens.

Materials/Specimens	Energy (kV)	Gun Current (μA)	Beam Angle	Sample Rotation (rpm)	Time (min)	Rocking
Tungsten plugs in IC cross sections.	≥ 6	250	Normal	10–20	3–6	None
Silicides in IC cross sections.	≥ 6	250	30°–45°	10–20	3–6	0–30°
Copper and tantalum contacts in IC cross sections milled by FIB systems.	6	300	35°	30	1–2	None
Aluminum/copper layers plus titanium and tungsten in FIB milled IC cross sections.	6	300	Normal	30	4	None
Copper pads and bond wires; proceed as follows:						
Step 1	6	300	45°	10	3	None
Step 2	6	300	Normal	10	7	None
MR heads.	5	200	Normal	10	1–2	None
Cleaved IC cross sections (for milling to pre-specified area).	≥ 8	≥ 350	Normal	10–20	Up to 15	None
Metallographic samples, proceed as follows:						
Step 1	8–10	350–400	45°–70°	10–20	Up to 10	None
Step 2	6–8	300	Normal	10–20	Up to 10	None
Iodine RIBE						
Tungsten plugs & transistors cross sections	6	200	Rocking	20	1.5	0–30°

Working on it…

Conductive coating

- Specimen need to be electrically conductive.
- Insulating samples build up an electrostatic charge.
- The charging leads to variations in surface potential:
  - Deflected secondary e^-
  - Increase secondary emission e^-
  - Deflection of electron beam
  - Spurious x-ray signal
- solution – coat the sample with a conductive layer.
- The coating must provide a path to ground.

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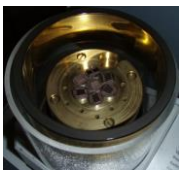
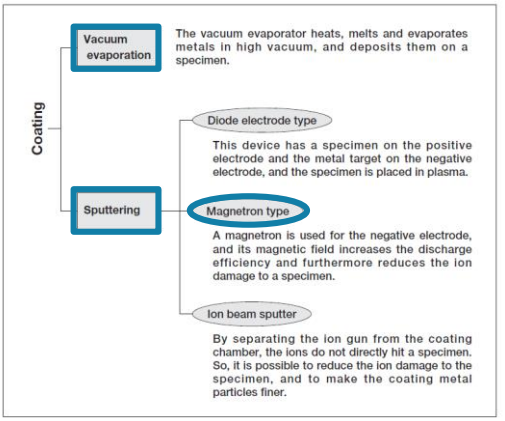
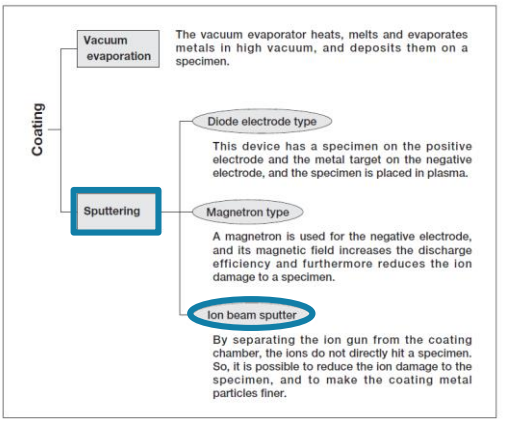


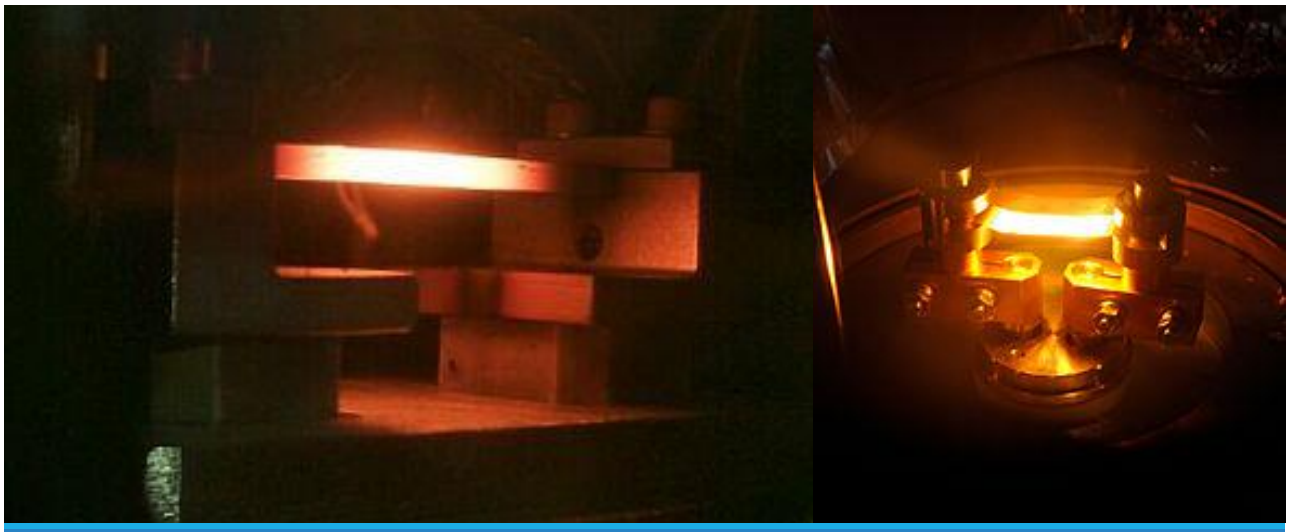
(Image: Manfred Kage)

Coating the sample – Balzers SCD/CED



Coating the sample - PECS





EVAPORATION

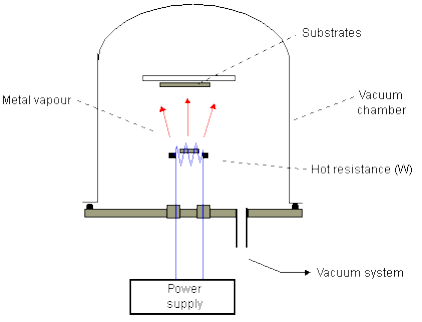
Evaporation

= transfer atoms from a heated source (which can be a liquid or a solid) to a substrate located a distance away to grow a film.

The source is heated directly or indirectly until the point is reached where it efficiently sublimes or evaporates.

When analyzing → evaporation rates and vapor pressure.

Other than pressure and temperature, the placement of the heater, source and substrate are important factors.

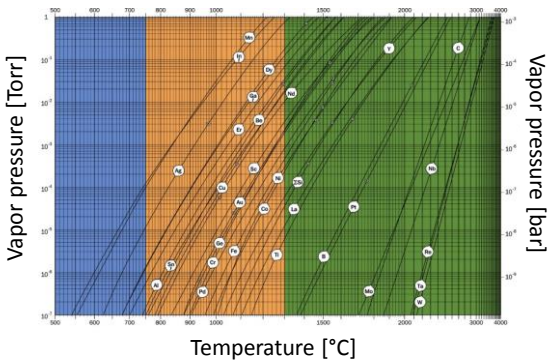


(Image: icmm)

Evaporation process

- place a suitable material inside the vacuum chamber with a heater
- seal and evacuate the chamber
- heat the source.
- when the temperature reaches the evaporation T, atoms or molecules start to leave the surface of the source and travel in more or less straight path until they reach another surface (substrate, wall)
- since these surfaces are at lower T, the molecules will transfer there energy to the substrate, lower their T and condense

Vapor pressure of elements



Below the vapor pressure surface evaporation is faster than condensation, above it it is slower.

The vapor pressure of any substance increases non-linearly with temperature according to the Clausius- Clapyeron equation: $\frac{dP}{dT} = \frac{\Delta H(T)}{T \Delta V}$

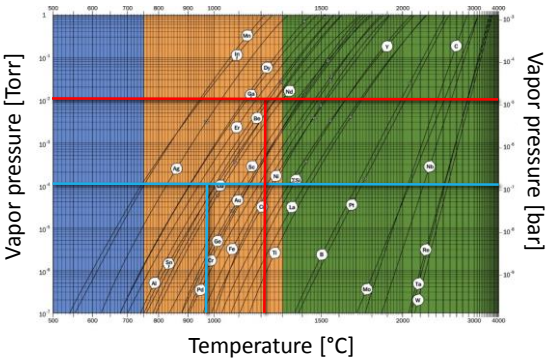
P – pressure,
T – temperature,
H – entropy,
V – specific volume

Mass evaporation rate:

$$\Gamma_e = 5{,}84 \cdot 10^{-2} \sqrt{\frac{M}{T}} P_v \frac{g}{cm^2 s}$$

M – molar mass
P_v – vapor pressure

Evaporation rate for aluminium



Al: M=27 g/mol

$P_v = 10^{-7}$ bar = 10^{-4} Torr → 980°C:

$$\Gamma_e = 5{,}84 \cdot 10^{-2} \sqrt{\frac{27}{980}} 10^{-4} \frac{g}{cm^2 s} = \mathbf{9{,}694 \cdot 10^{-7}} \frac{g}{cm^2 s}$$

$P_v = 10^{-5}$ bar = 10^{-2} Torr → 1220°C:

$$\Gamma_e = 5{,}84 \cdot 10^{-2} \sqrt{\frac{27}{1220}} 10^{-2} \frac{g}{cm^2 s} = \mathbf{8{,}688 \cdot 10^{-5}} \frac{g}{cm^2 s}$$

Deposition rate

Not only related to the **evaporation rate** but also to the **angle** and **distance** between the source and substrate.

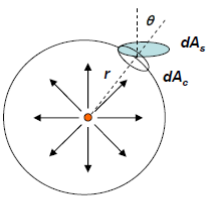
Assumption: ballistic regime and the evaporated atoms travel in a straight line from the source to the substrate.

We are interested in the mass lost from the source:

$$M_e = \int_0^t \int_{A_e} \Gamma_e dA_e dt$$

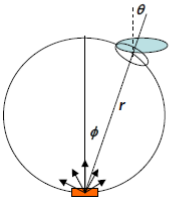
Where A_e is the surface area of the source.

Point Source

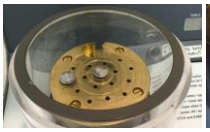


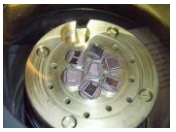
$$\frac{dM_s}{dA_s} = \frac{M_e \cos\theta}{4\pi r^2}$$

Surface Source



$$\frac{dM_s}{dA_s} = \frac{M_e (n+1) \cos^n \phi \cos\theta}{2\pi r^2}$$





Sources of impurity

What can effect film purity?

Contamination of source materials

- use high purity of source material

Contamination of the heater

- use material with low diffusion

Residual gas in the chamber

- better vacuum, higher deposition rate

(Image: wiki)

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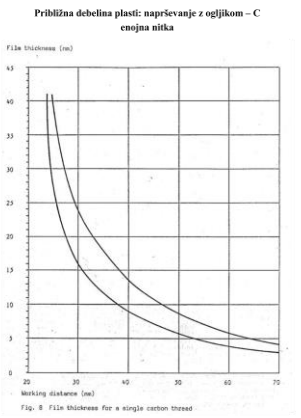
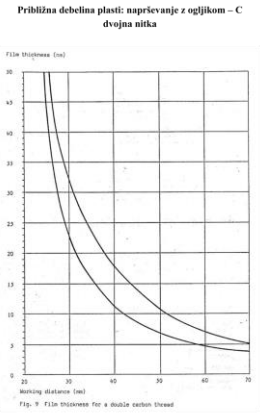
(Image: lasp)

Film thickness variation - SCD

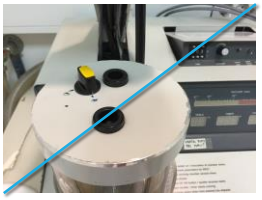
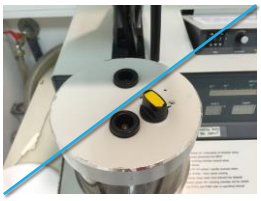


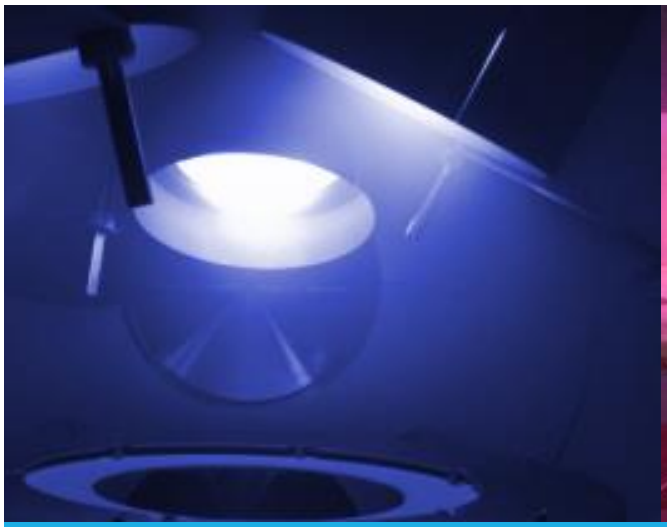
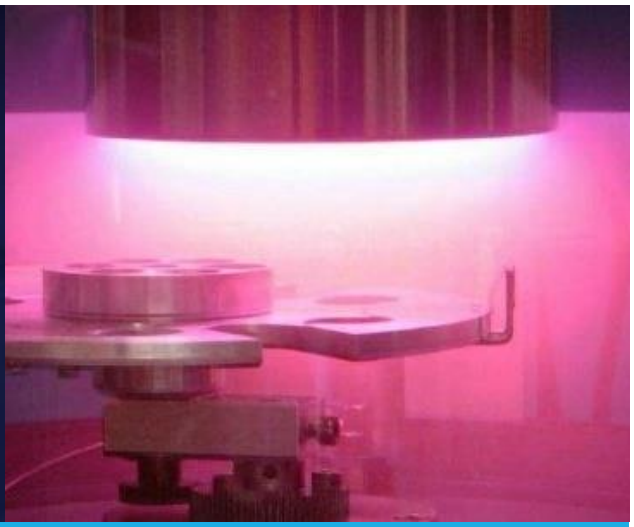


The values only apply when the carbon thread has been sufficiently degassed and the working distance and pressure are held to.

The film thickness is also a function of factors such as transfer resistance at the clamping head and the resistance of carbon thread itself. Thus deviations can occur.

Also note that the film thickness values are given for the center of the specimen table. And they decrease towards the edge of the table.

SPUTTERING

Sputtering

Instead of using heat to eject material from a source, we can bombard them with high speed particles.

The momentum transfer from the particles to the surface atoms can impart enough energy to allow the surface atoms to escape.

Once ejected, these atoms (or molecules) can travel to a substrate and deposit as a film.

Figure removed for copyright reasons.

(Image: alyssahale)

Sputtering process

Figure removed for copyright reasons.

(Image: micro magnetics)

- the target material and the substrate is placed in a vacuum chamber
- a voltage is applied between them so that the target is the cathode and the substrate is attached to the anode
- a plasma is created by ionizing a sputtering gas (generally a chemically inert, heavy gas like Argon)
- the sputtering gas bombards the target and sputters off the material we would like to deposit

Generating and controlling the plasma

Ions can be generated by the collision of neutral atoms with high energy electrons.

The interaction of the ions and the target are determined by the velocity and energy of the ions.

Since ions are charged particles, electric and magnetic fields can control these parameters.

The process begins with a stray electron near the cathode is accelerated towards the anode and collides with a neutral gas atom converting it to a positively charged ion.

The process results in two electrons which can then collide with other gas atoms and ionize them creating a cascading process until the gas breaks down.

$$e^- + A = 2e^- + A^+$$

The breakdown voltage depends on the pressure in the chamber and the distance between the anode and the cathode.

At too low pressures, there aren't enough collisions between atoms and electrons to sustain a plasma.

At too high pressures, there so many collisions that electrons do not have enough time to gather energy between collisions to be able to ionize the atoms.

Figure removed for copyright reasons.

(Image: Roman Pyshchyk.)

Plasma pressures

Unless there are enough collisions, the plasma will quickly die.

In order to have a self-sustaining plasma, each electron has to generate enough secondary emission.

Since we want collisions to occur, the pressure can not be too low. The mean free path should be a tenth or less than the typical size of the chamber.

Also, since we want the electrons to gain enough energy between collisions, the pressure can not be too high.

Ion-surface interactions

When ions bombard a surface, several things can happen:

- Adsorption (sticking),
- Elastic scattering (reflection),
- Sputtering,
- Ion implantation,
- Chemical reactions, …
- Electron and photon emission

The ion beam energy is the critical parameter:

- < 5 eV : Adsorption or reflection
- 5 - 10 eV : Surface damage and migration
- **3 - 10 keV** : Sputtering
- > 10 keV : Ion implantation

Figure removed for copyright reasons.

(Image: AG Weitzel, Uni Marburg)

How ions sputter atoms?

When ions collide with surface atoms on the target, the energy transfer can knock some of these atoms off the surface.

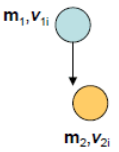
The key principle is energy ($K = \frac{1}{2}mv^2$) and momentum ($p = mv$) conservation.

In any collision, momentum is conserved.

If the collision is elastic, kinetic energy is also conserved.

The energies required for sputtering are much higher than lattice bonding or vibrational energies (which are the causes of inelastic interactions), therefore sputtering collisions can be considered elastic.

Indicial point:



$$K_i = \frac{1}{2}(m_1 v_{1i}^2 + m_2 v_{2i}^2)$$

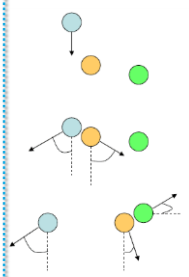
$$p_i = m_1 v_{1i} + m_2 v_{2i}$$

Final point:

$$K_f = \frac{1}{2}(m_1 v_{1f}^2 + m_2 v_{2f}^2)$$

$$p_f = m_1 v_{1f} + m_2 v_{2f}$$

Elastic: $K_i = K_f \qquad p_i = p_f$

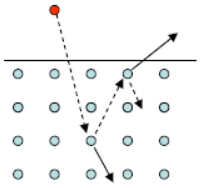


For normal incidence of ion, the primary collision can not eject an atom off the surface. However, the secondary collision can!

Sputtering regimes

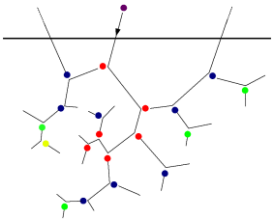
Single Knock-On (low energy)

The initial ion-surface collision sets target atoms in motion. If enough energy is transferred, binding forces can be overcome. Typical threshold energies are in the 10 - 30 eV range.



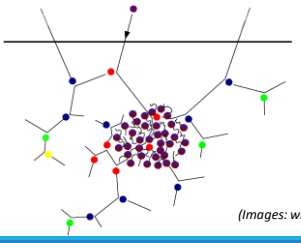
Linear Collision Cascade (medium energy)

At higher ion energies (100 eV - 10 keV) recoil is minimal and a cascading effect produces sputtering



Thermal Spike (high energy)

The collisions between the ions may occur so near to each other that they can not be considered independent of each other.



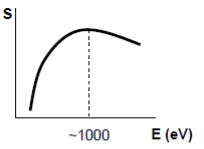
(Images: wiki)

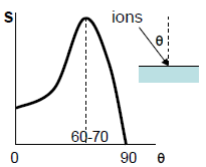
Sputtering yield – S [atoms/ions]

Number of ejected (sputtered) atoms, molecules from target divided with the incident particle, ions

$$S = \frac{Number\ of\ sputtered\ atoms}{Number\ of\ incident\ ions}$$

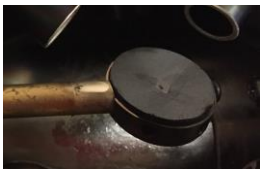
Namigi:
C: 8-9 keV, L&D 350 µA, 0,2 - 0,4 Å/s,
min 4 nm (2 min) **max 8 nm** (4 min)
Au/Pd: 6-7,5 keV, L&D 200 - 220 µA, 1,2 - 1,3 Å/s,
min 3 nm (25 s) **max 6 nm** (50 s)
Pt: 6-7 keV, L&D 200 - 220 µA, 0,7 – 0,8 Å/s,
min 3 nm (40 s) **max 6 nm** (80 s)
Cr: 6-7 keV, L&D 200 µA, 0,5 – 0,7 Å/s,
min 3 nm (1 min) **max 8 nm** (2,5 min) + **LN_2 past**





S depends on:

1. type of target atom and the binding energy
2. relative masses (of ions and atoms)
3. angle of incidence of ions and kinetic energy



Deposition

Sputtered atoms from the target make their way on to the substrate through diffusion.

Ions and neutralized gas atoms may also embed on the substrate as impurities.

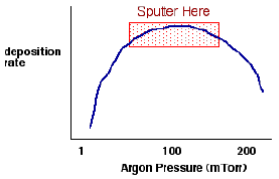
The ions incident on the substrate may also re-sputter the surface.

Chemical reactions may occur.

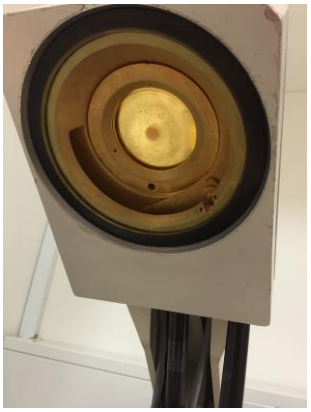



Deposition rate is proportional to the sputtering yield. An optimum pressure exists for high deposition rates.

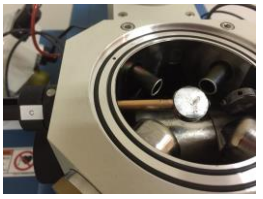
- Higher pressure means more collisions and ions.
- Lower pressure means less scattering.

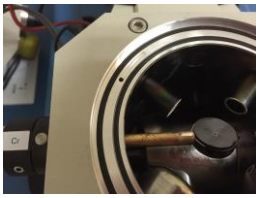
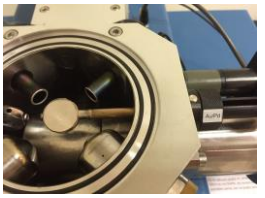


Targets on SCD and PECS

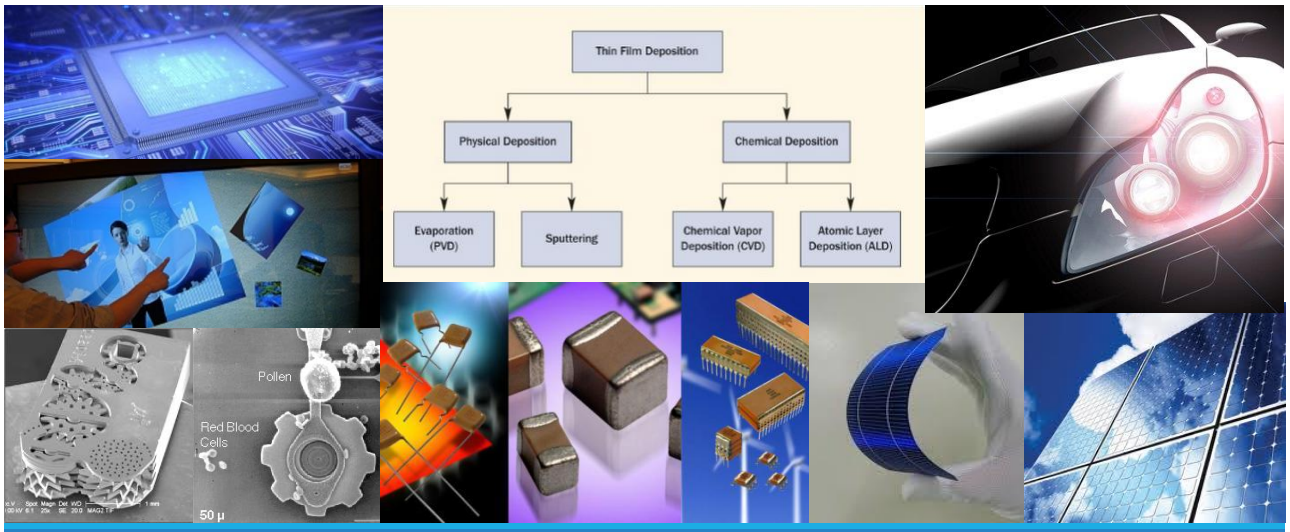



Magnetron target (Au, Pt) demonstrating racetrack erosion profile



PECS targets (Cr, Au/Pd, C and Pt)



Thin film growth

Physical mechanisms of thin film growth

Članek!!

Video removed for copyright reasons.

(1) Volmer-Weber: (island growth):

M. Volmer and A. Weber, *Z. Phys. Chem.* **119**, p. 277 (1926).

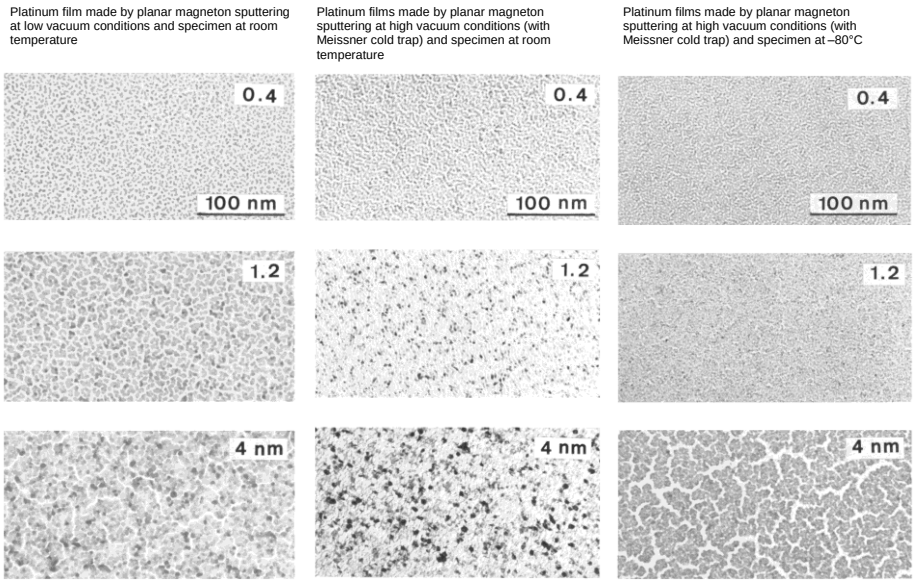
(2) Frank-Van der Merwe: (layer growth; ideal epitaxy):

F. C. Frank and J. H. Van der Merwe, *Proc. R. Soc. London*, Ser. A **198**, p. 205 (1949).

(3) Stranski-Krastanov: (layers + islands):

J. N. Stranski and L. Krastanov, *Ber. Akad. Wiss. Wien* **146**, p. 797 (1938).

(Video: Barna, 1967)



[T.Müller *et. al.* Cryo-Preparation and Planar Magneton Sputtering for low Temperature Scanning Electron Microscopy; Scanning Electron Microscopy Vol. 4, (1990)]

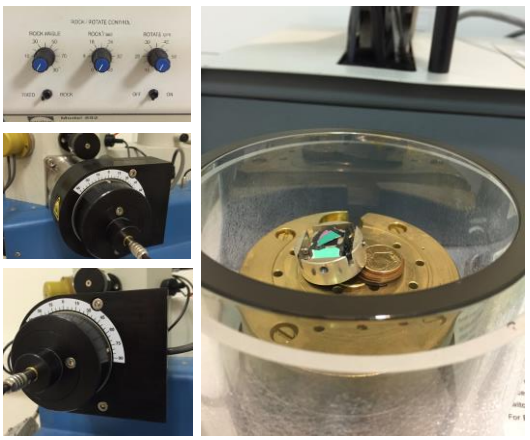
Film uniformity

Angular distribution of sputtering depends on the pressure.

Lower pressures result in a more directed flow which results in less uniform films.

Higher pressures result in more isotropic flow and better coverage.

Uniform films also require larger targets.



Thickness measurment

Gravimetric method

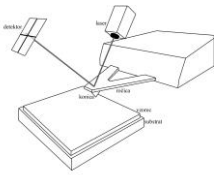
- Measure substrate weight before and after coating
- Calculate thickness from known substrate dimensions
- Not real-time but surprisingly accurate

(Image: wiki)

Stylus method – profilometer or AFM:

- A stylus is drawn across a step in the film
- Scratching can occur
- Needs calibration
- Can do repeated measurements
- Not real-time

Figure removed for copyright reasons.



(Image: l-w)

Thickness measurment

Quartz crystal monitors - Quartz oscillator

Specific oscillation frequency

Expose one side of wafer to the vapor

As the vapor coats the wafer the oscillation frequency changes

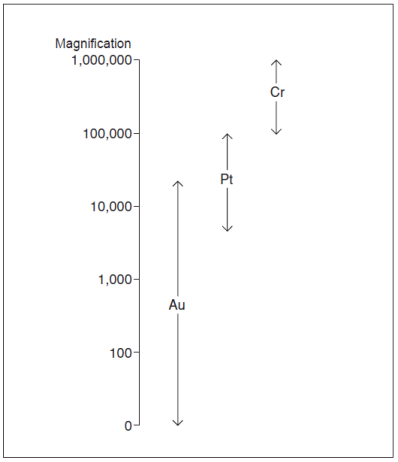
Different parameters, proper calibration, quartz quality and proper usage

If 6MHz oscillator is used – nanogram changes can be measured in turn that means to 0,1A

Figure removed for copyright reasons.

(Image: lesker)

What material should I coat with?



Au: standard for sputtering, easy to coat, inert, stable under electron beam

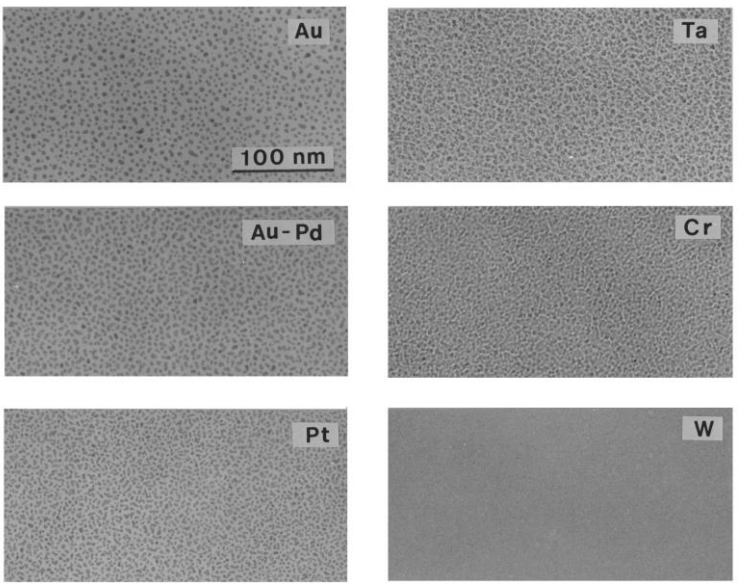
Au/Pd: all the advantages of Au bus smaller grain size

Pt: highly inert, very conductive but large grain size

Cr: smallest grain size, but oxides quickly

C: best for X-ray microanalysis and EBSD

Influence of the Coating Material to the Quality



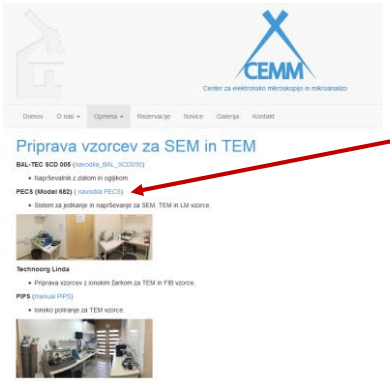
0.4 nm nominal film thickness (magnetron sputter) coatings produced at room temperature at low vacuum conditions

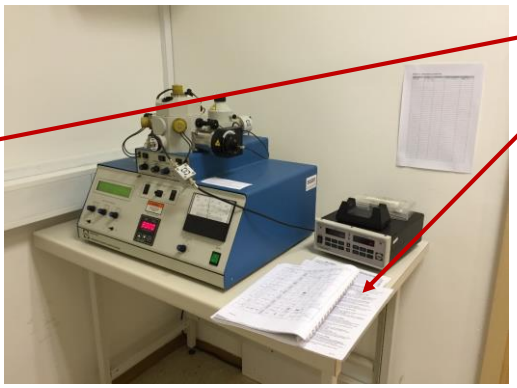
Practical part

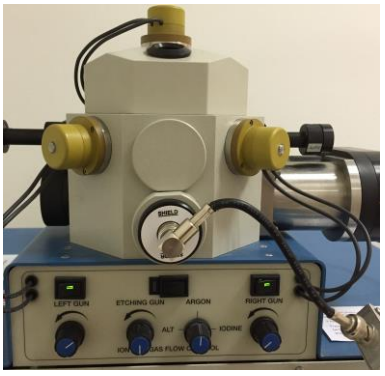
CEMM web site

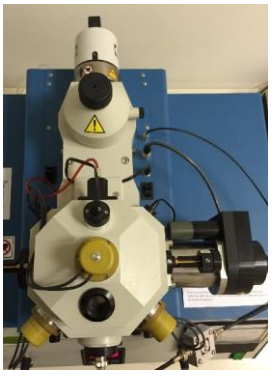
Precision etching coating sistem – PECS 682

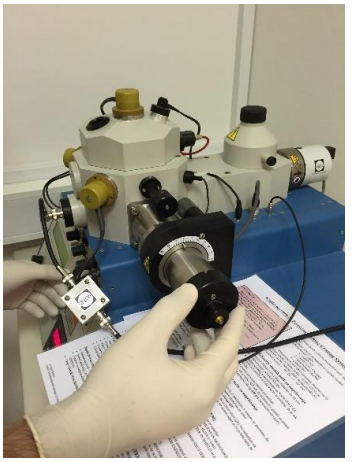
instructions are on the web site and on the table were PESC is



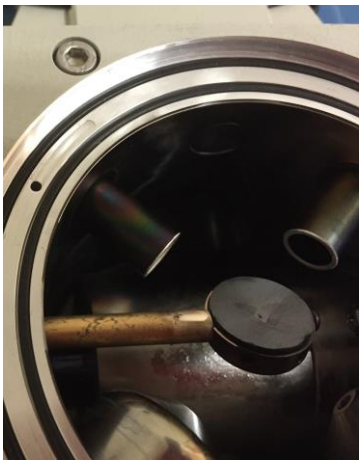


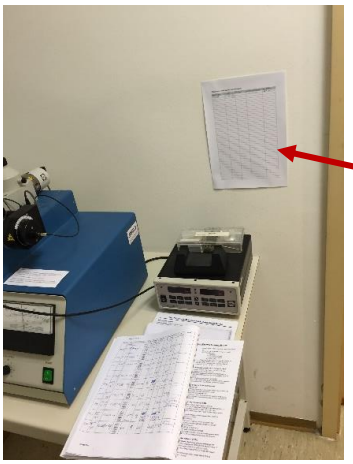






Do not push it to much!





Kratka navodila za Precision Etching Coating System

OPOZORILA

- **Vzorci morajo biti POSUŠENI, SPIHANI, brez delcev, ki bi jih lahko vakuum potegnil v sistem!**
- **Nikoli naj ne bo napetost 10 keV (izjema jedkanje)**
- **Nikoli ne smejo tokovi presegli 425 µA!!**
- Ko začneš z delom preveri, da je tlak < 10^{-3} Pa
- Ne dotikaj se notranjega dela nosilca in obvezna uporaba rokavic!
- **Obvezno čiščenje holderja z zobotrebcem!**
- Ko klikaš VENT/VAC vedno počakaj, da lučka ugasne in šele potem ponovno klikni gumb!
- Ne pritiskaj VENT tipke dokler ni nosilec z vzorci zunaj, sicer podreš vakuum komore!
- Preberi navodila proizvajalca!
- Preveri, da je pretok argona 5 bar.

Začetne nastavitve

- Napetost je vključena (zeleno stikalo)
- Vakuum < 10^{-3} Pa
- Predvakuum mehanska črpalka (črtelina)
- Hitrost turbomolekularne črpalke (~ 24000 rpm)
- HT napetost izključena (ne sveti rdeča lučka)
- HT potenciometer na 0
- Napršcvalni ionski puški: OFF
- Jedkalna ionska puška: OFF
- Plin: Argon
- Shutter zaprt (vijak spodaj)
- Kvarčna tehnica zaprta (položaj shield)
- Razsvetljava komore izključena

Vstavljanje vzorca

- Izključijen nagib vzorca (stikalo na FIXED)
- Potenciometra za kot in hitrost nagibu na minimum (ROCK)
- Izključena rotacija (stikalo »ROTATE« OFF)
- Potenciometer za hitrost rotacije na minimum (ROTATE)
- Izvaki kabel za rotacijo vzorca
- Premakni stikalo »AIRLOCK CONTROL« na »OUT«
- Ko pride nosilec ven klikni »VENT«
- Nosilec previdno vzameš ven (pazi oring!).
- PREVERIŠ O-RING! Lupa!!
- Vstaviš adapter z vzorci.
- RAHLO potisneš nosilec noter in pazi, da gre zareza v zatič
- Klikni »VAC«
- Premakni stikalo »AIRLOCK CONTROL« na »IN«
- Priklopi kabel za rotacijo vzorca

Nastavitve na napršcvalniku

- Vakuum naj bi bil < 10^{-3} Pa
- Shutter (zaslonka) ZAPRT (vijak gleda dol) – lučka
- Detektor za merjenje debeline zaprt - polożaj »SHIELD«
- Vklopi **THICKNESS MONITOR**

– Kliknes gumb »STOP« (resetiraš P fail) –gori zelena luč

– Kliknes »FILM NUMBER« in z gumbi modify izbereš številko tarče:

1 = eglijk (C)
2 = krom (Cr) +LN_2 past
3 = zlato/paladij (Au/Pd)
4 = platina (Pt)

– Kliknes gumb »START« (resetiraš debelino na 0)

- Vklopi stikala za ionske puške – »LEFT GUN« in »RIGHT GUN« (vakuum pade, zaradi pretoka Ar. Vrednost je med $1 \cdot 10^{-2}$ Pa – $5 \cdot 10^{-2}$ Pa)

Stabilizacija ionskih pušk za napršcvanje

- Nastavi »HIGH VOLTAGE TIMER« na 30 min
- Kliknes gumb »START/STOP«
- **Počasi povečuj** potenciometer na NAPETOST ZA NAPRŠEVANJE (od 6 do 9 keV) in počakaj, da je tok stabilen
- Po potrebi spremeni pretoke pri puškah.
- Max. tok je lahko 425 µA, če ni nastavi z gumbi za pretok plina. Optimalno okrog **350 µA** (trajanje nrszpara)

Vstavljanje tarče za napršcvanje

- **Izklopi HT**
- Izberemo tarčo in jo potisnemo v komoro in zavrtimo, da je nalepka z oznako materiala na vrhu!
- Ko je vstavljena **vklopi HT!**
- Počakamo 1 min, da se tarča očisti (gle) list nalepljen na steni, kjer piše ali je bil sistem odprt in če je bila tarča že očiščena!)

Napršcvanje vzorca (SEM)

- Po želji vklopiš nagib vzorca in rotacijo
- Preveri, da je debelina na THICKNESS MONITORJU 0 sicer pritisni gumb »START« (0,01kA=1nm)
- ISTOČASNO obrneš SHUTTER IN SHIELD in zapiši čas.
- Ko doseżeš željeno debelino zapreš SHUTTER in **zapiši čas v zvezek**
- Zapreš SHIELD
- Zniżaš potenciometer »BEAM ENERGY« na 0kV
- Izvlečeš tarčo (vijak na vrhu in potegneš ven)
- Izklopi ionski puški
- Izklopi ROCK in ROTATE
- Ugasneš THICKNESS MONITOR
- Kliknes »START/STOP«, če se ni že sam ugasnil. Držiš START/STOP, da postaviš timer nazaj na 30 minut.

Napršcvanje vzorca (TEM)

- **Vzorec vstaviš v holderjem (razen analitskega!!!)**
- Preveri, da je debelina na THICKNESS MONITORJU 0 sicer pritisni gumb »START« (0,01kA=1nm)
- ISTOČASNO obrneš SHUTTER IN SHIELD in zapiši čas.
- Ko doseżeš željeno debelino zapreš SHUTTER in **zapiši čas v zvezek**

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Maj 2015

TEM coating with SCD, CED and PECS