CONSULTING LTD

Flexible Barrier Materials

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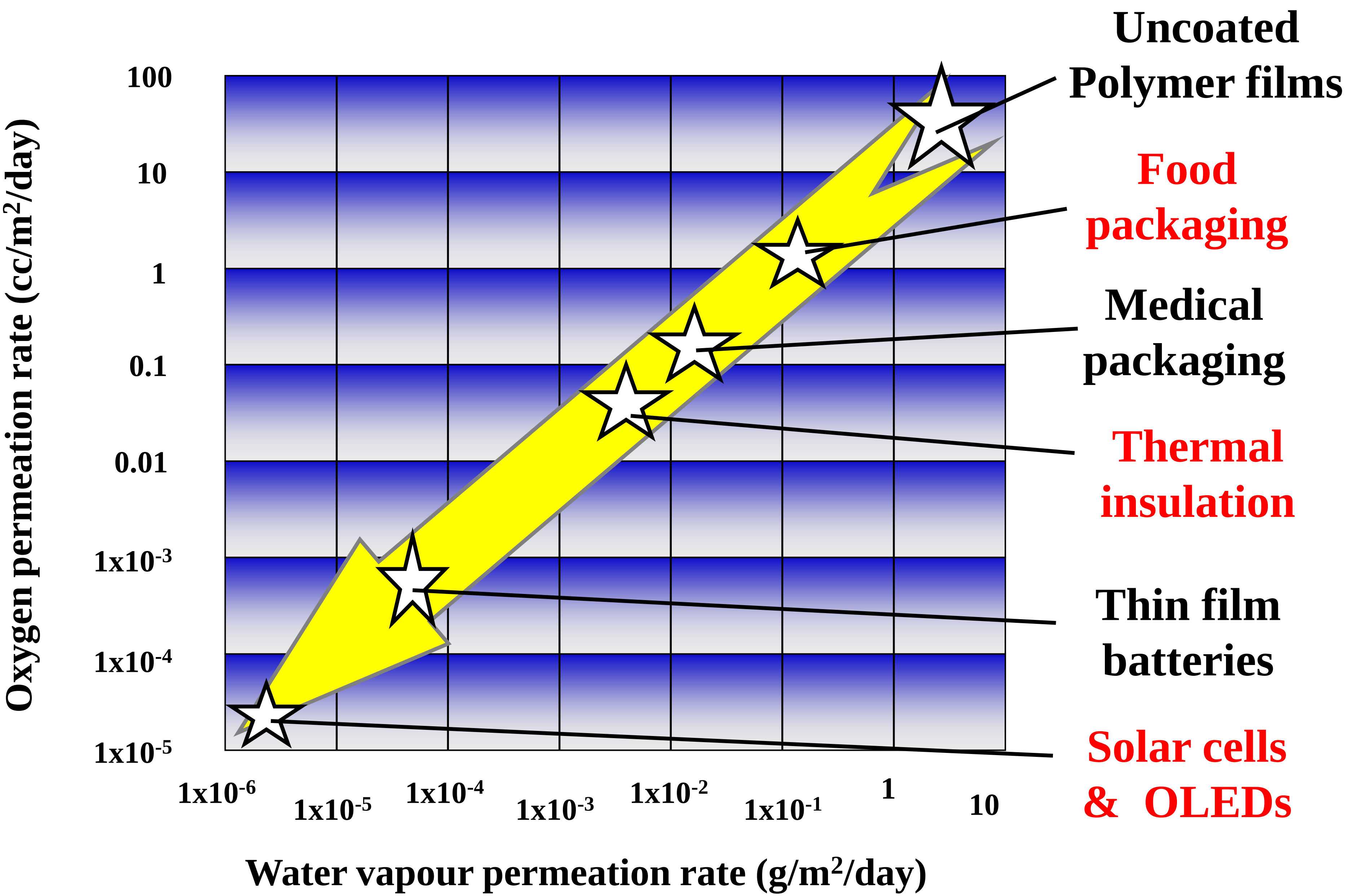
Barrier materials

Range of barrier performance



Properties

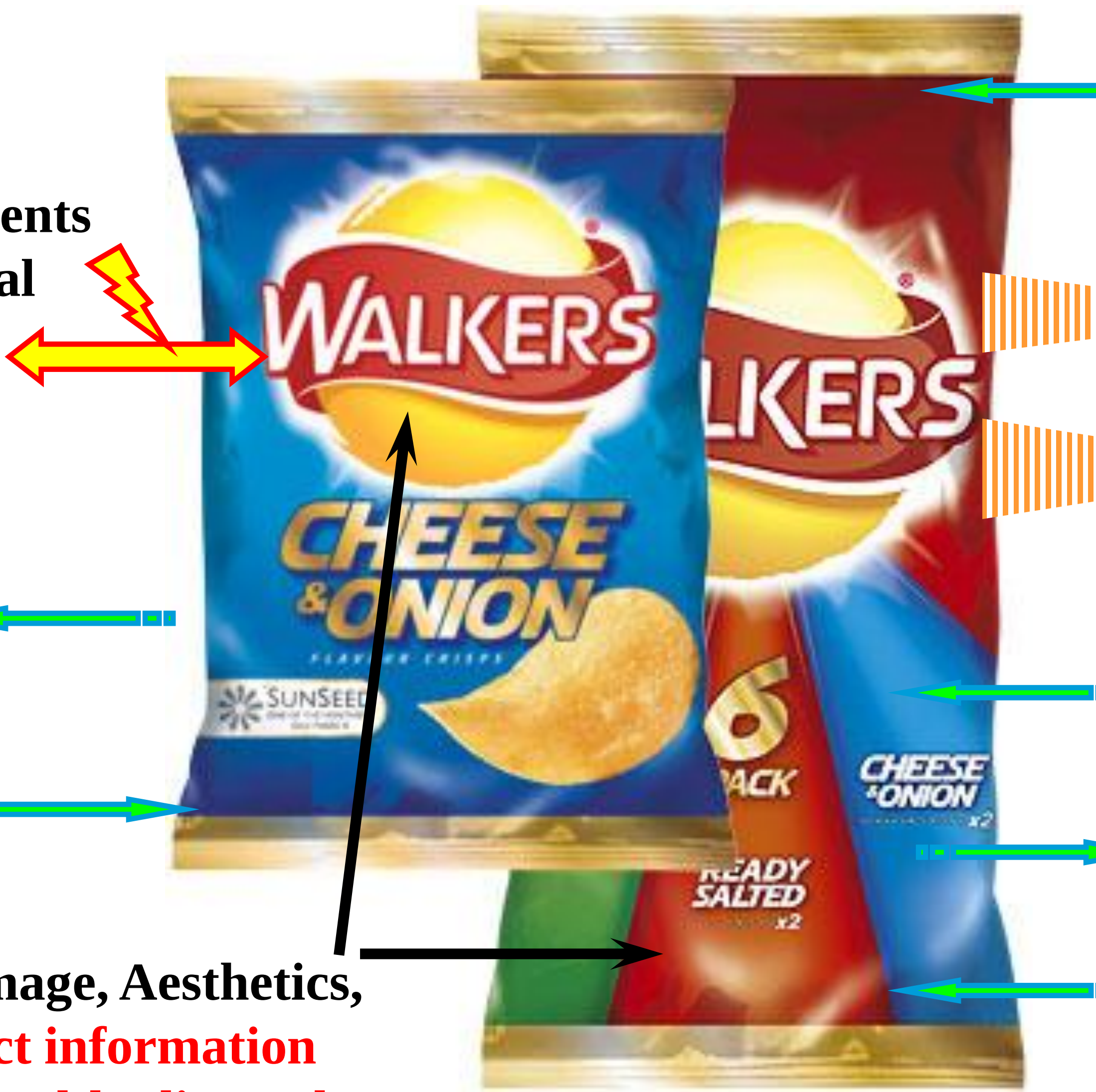
Light barrier
Moisture barrier
Gas (Oxygen) barrier
Odour / taint barrier
Modified Atmosphere Packaging - CO_2 - ethylene – etc

Chemical / biological / anti-bacterial / anti-microbial / antiseptic
EMI/RFI screening, Anti-static
Decorative / aesthetics / convenience
Mechanical – containment – heat seal – puncture resistance

Food Degradation

Rancid – fats affected by light & oxygen
Soggy – moisture absorption
Taint - loss of flavour or alteration of aroma
Loss of colour
Loss of texture – bloom on surfaces
Degradation – mould growth, chemical interaction, etc

Total packaging performance



Physical properties to form package – e.g. heat seal

Protect contents from physical damage

Light, UV degradation i.e. rancidity

Flavour loss out

Moisture in

Taint in

Modified gas atmosphere out

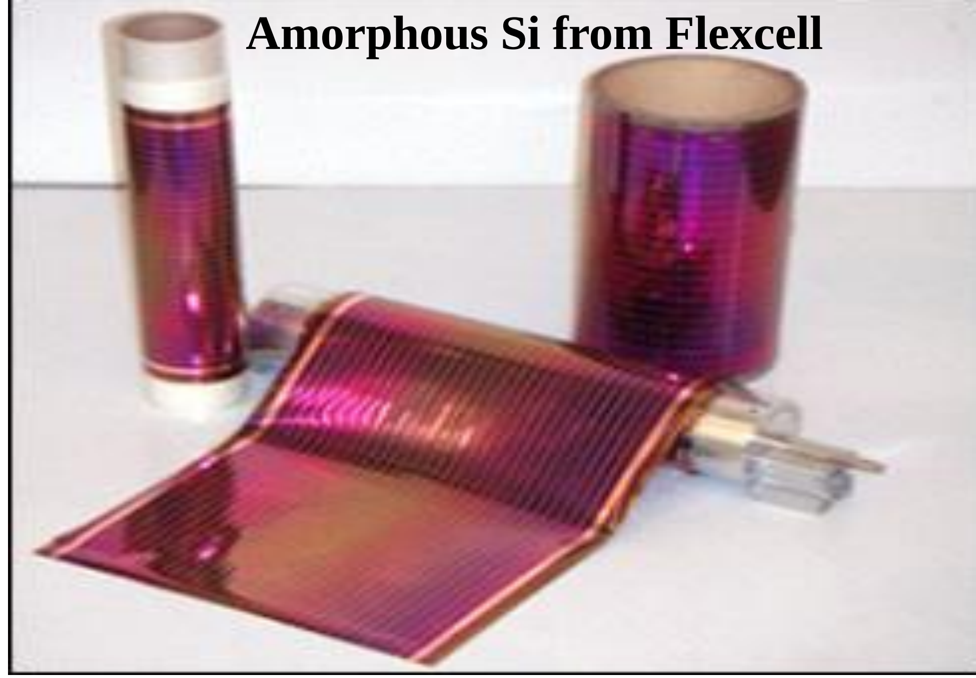
Oxygen in

Brand image, Aesthetics,

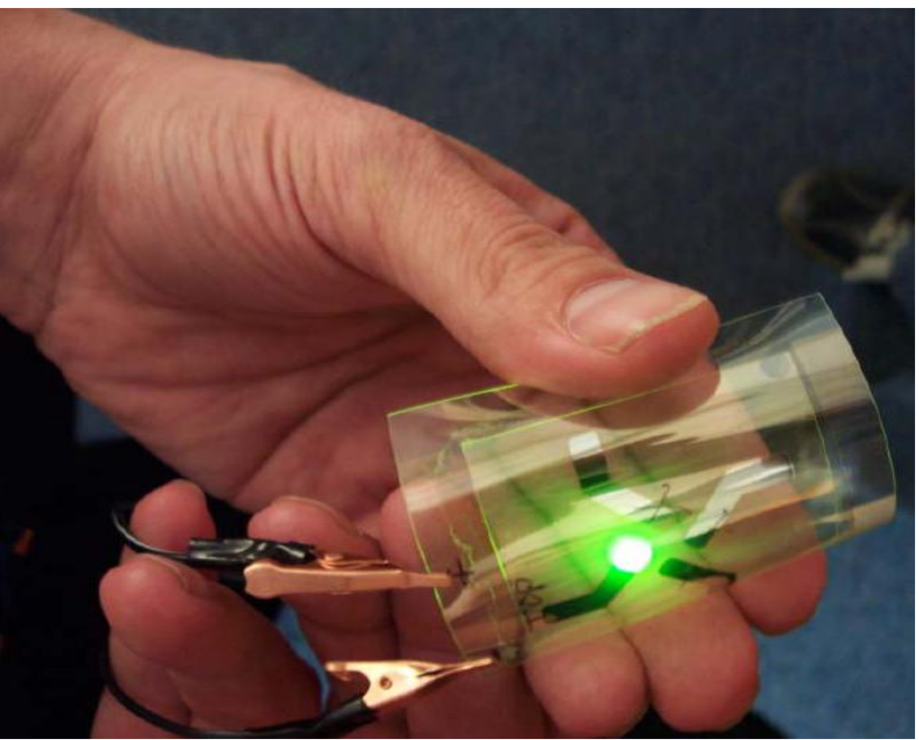
Product information

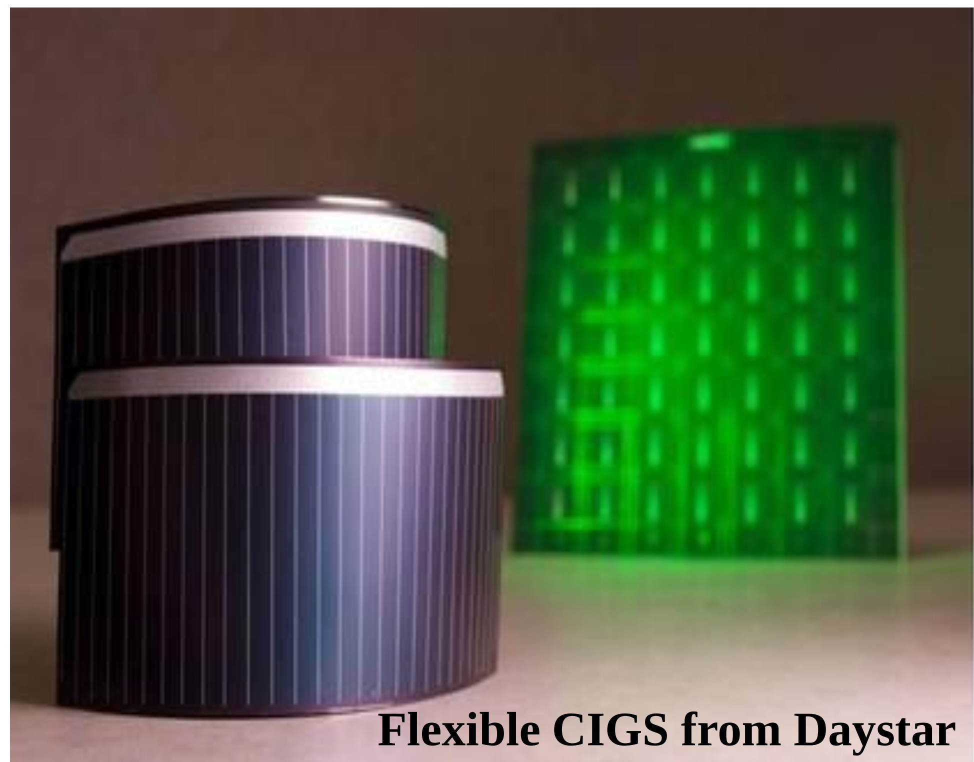
Contents, health, disposal, etc

General Atomics OLED demonstration devices



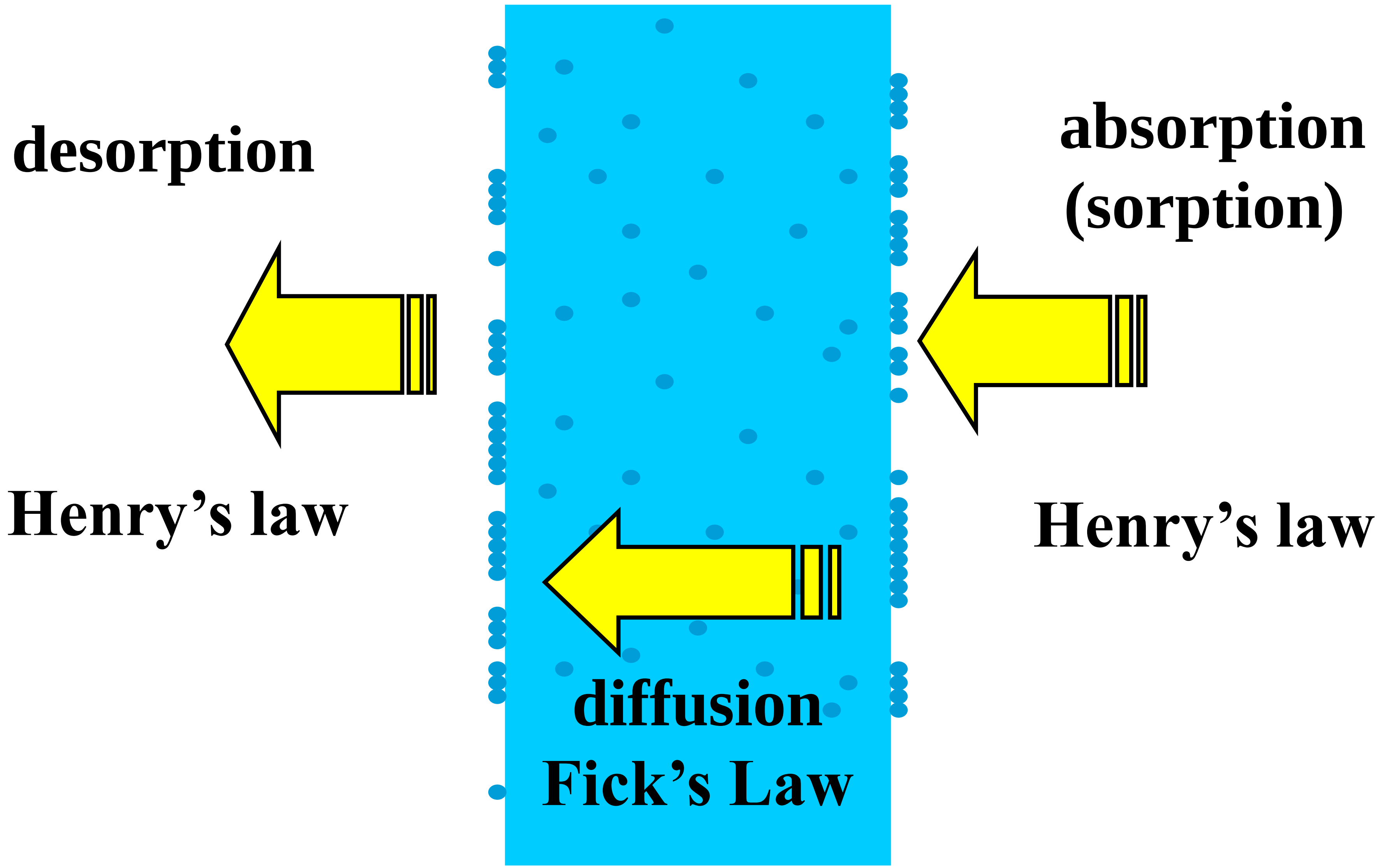
Amorphous Si from Flexcell





Flexible CIGS from Daystar

Permeation

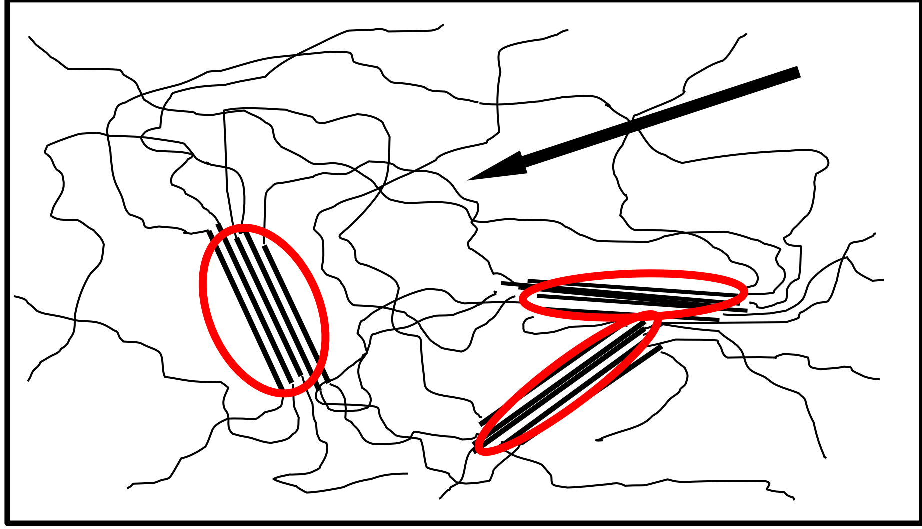

desorption
Henry’s law
absorption
(sorption)
Henry’s law
diffusion
Fick’s Law

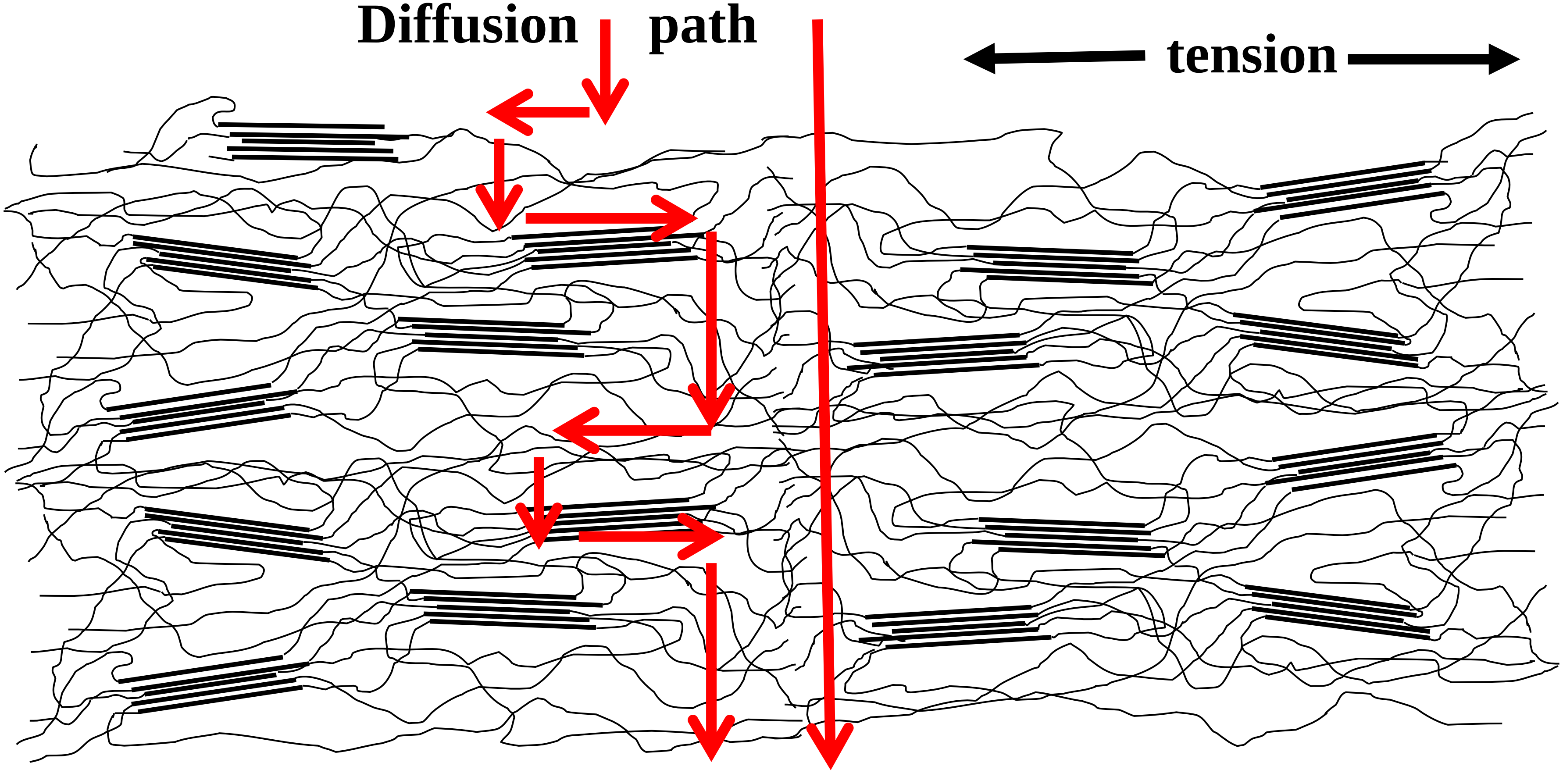
Diffusion coefficients

Diffusion Coefficients

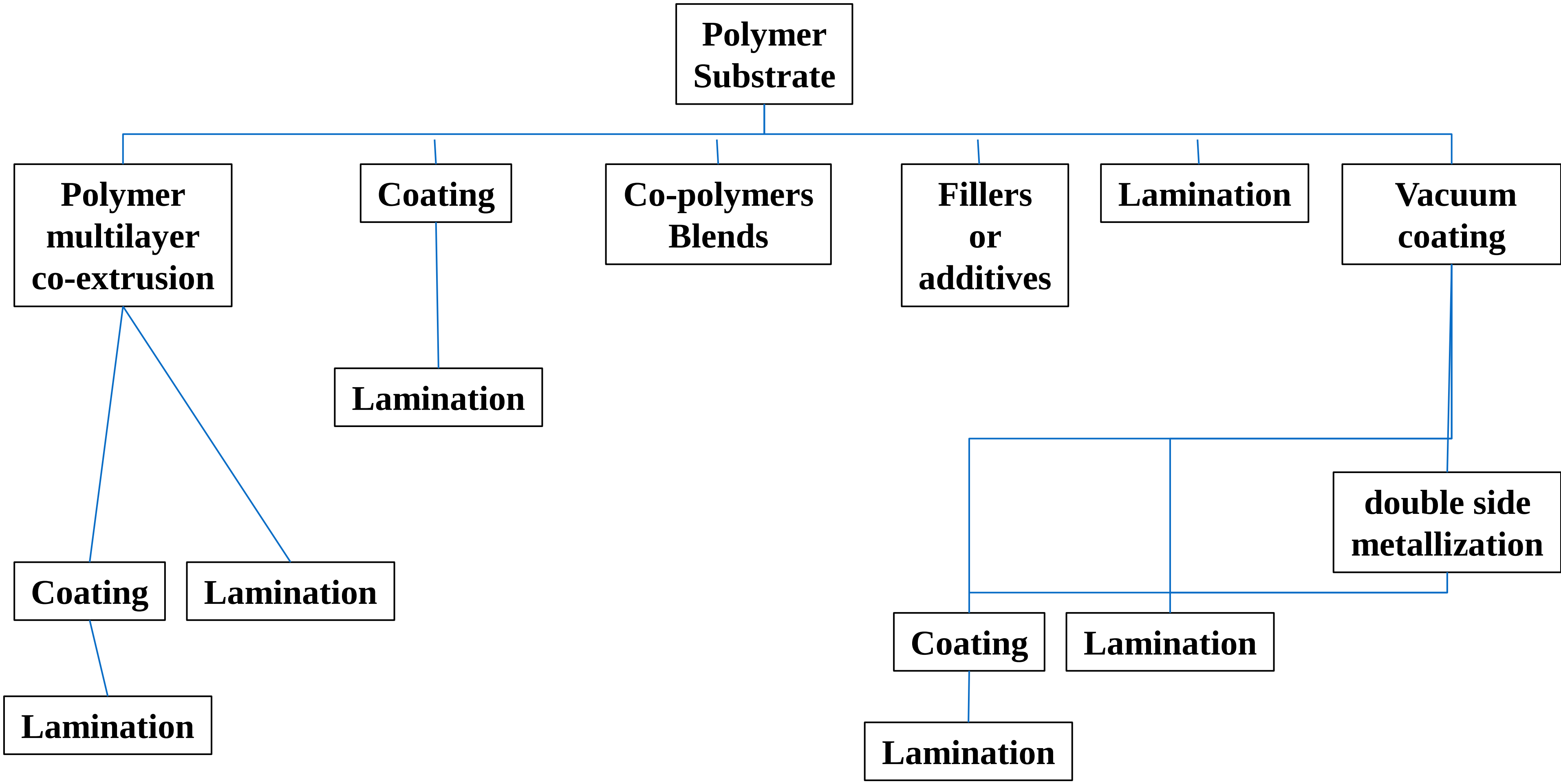
Oxygen in air	D_{O2} = 0.15 cm^2/s
Oxygen in Water	D_{O2} = 2 x 10^{-5} cm^2/s at 20°C
Oxygen in Quartz	D_{O2} = 10^{-25} cm^2/s
Oxygen in Silica	D_{O2} = 10^{-13} cm^2/s
Oxygen in Silica Gel	D_{O2} = 10^{-3} cm^2/s
Oxygen in Polypropylene	D_{O2} = 10^{-7} cm^2/s
Oxygen in Polyester	D_{O2} = 10^{-9} cm^2/s
Water vapour in air	D_{H2O} ≈ 0.26cm^2/s

Biaxial substrates





Basic structures

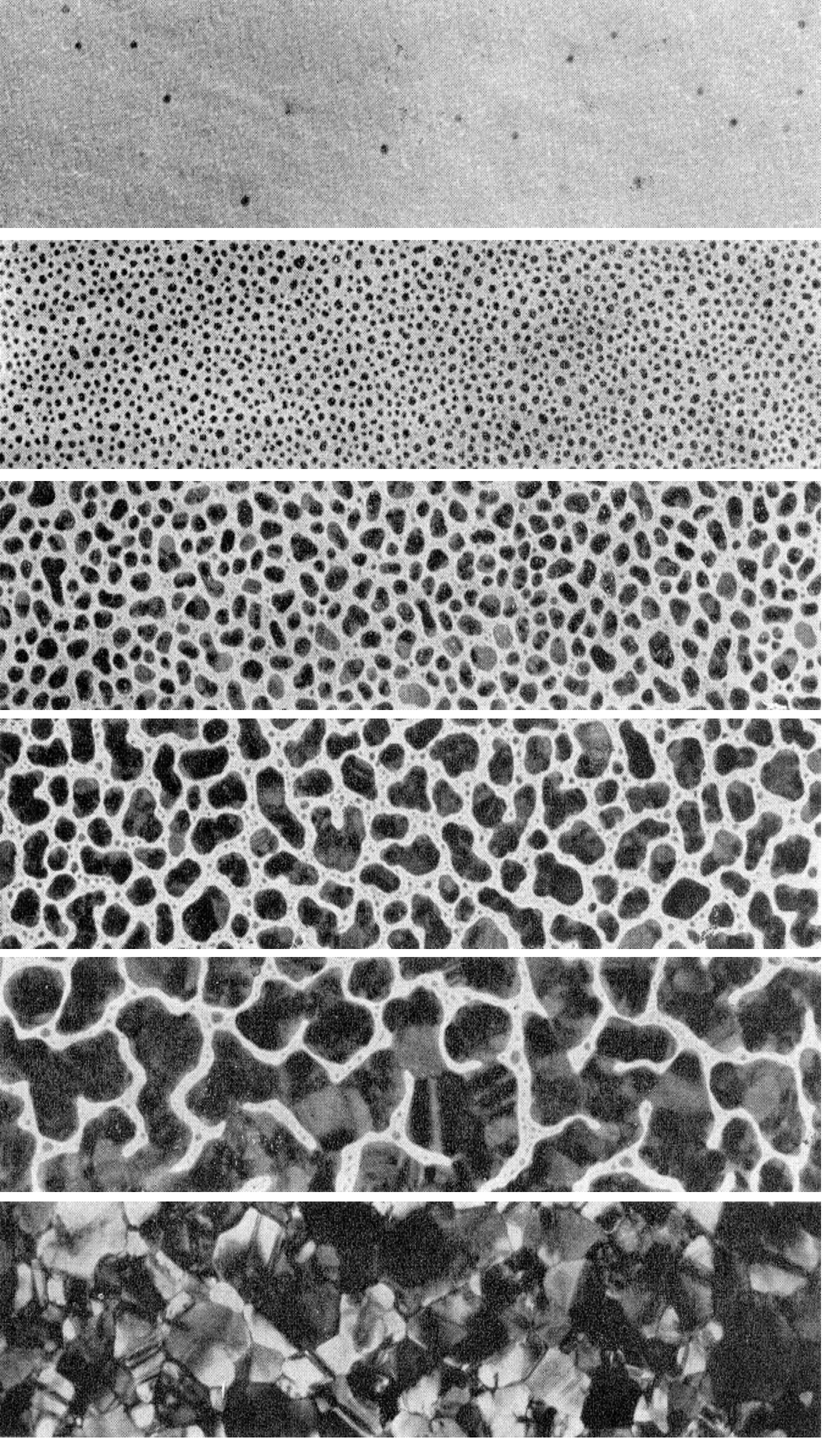


Polymers or coatings can be with or without fillers

Barrier performance

- **Performance of multi-layers dependent upon:-**
- **Adhesion**
  - **Dependent upon surface roughness, quality & cleanliness**
  - **Dependent upon surface energy & wetting (wetting ≠ adhesion)**
  - **Dependent upon amount & type of surface treatment**
  - **Dependent upon chemical bonding**
- **Quality of materials, coating technique & handling**
  - **Including filtration of coatings**
  - **Density of coatings**
    - **Dependent upon deposition process**
- **Minimise handling – protect fragile coatings**

Nucleation
&
Film Growth



0.001nm

0.5nm

3.0nm

6.0nm

15 nm

50 nm

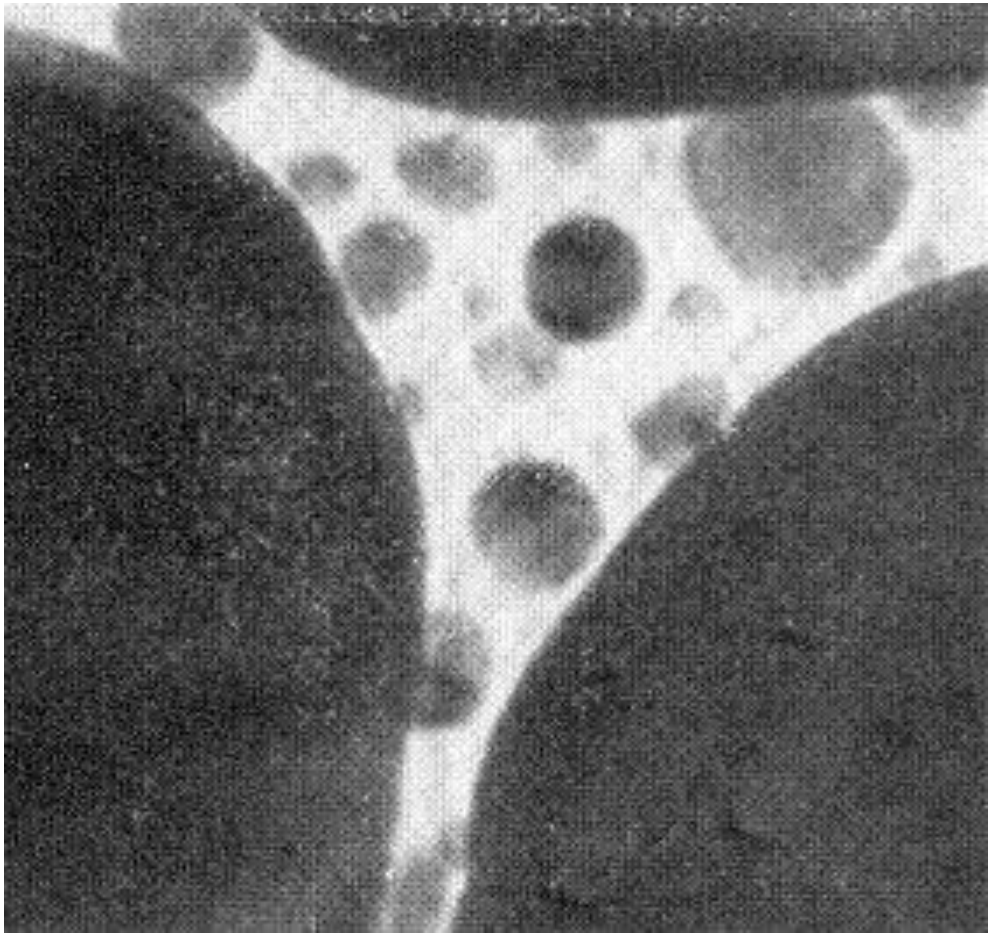
Gold nucleating onto glass

Transmission Electron Micrographs (TEM) 75,000x Magnification

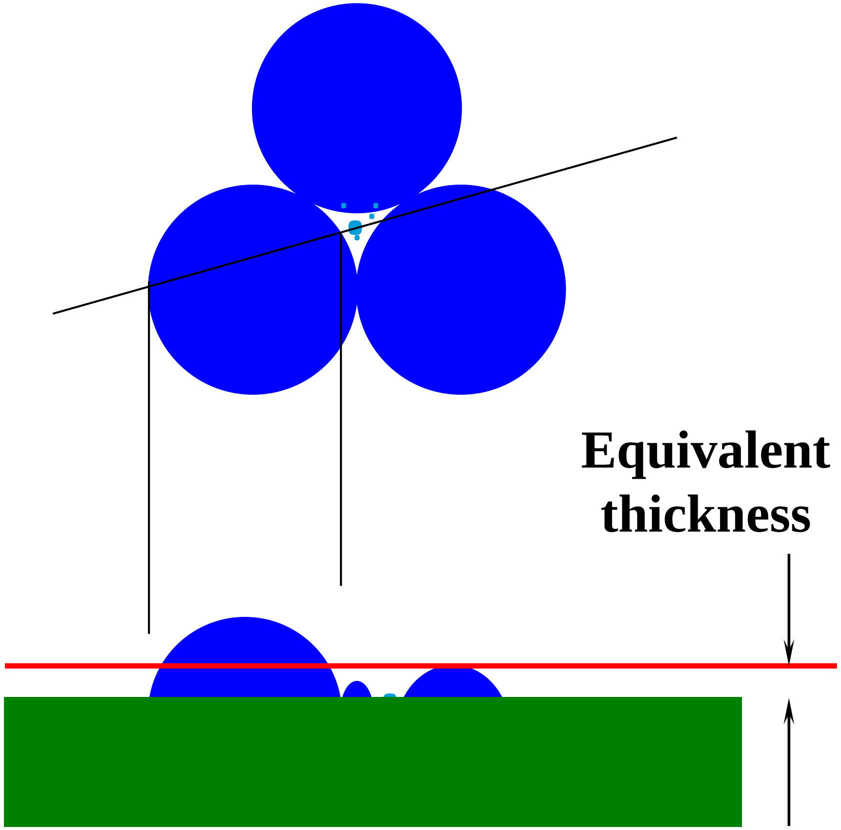
The thickness indicated is for a film of equivalent mass that is continuous & parallel

R.M.Hill
Contemp Phys. 1969 Vol 10 No 9 pp 221-240

Nucleation & Film Growth

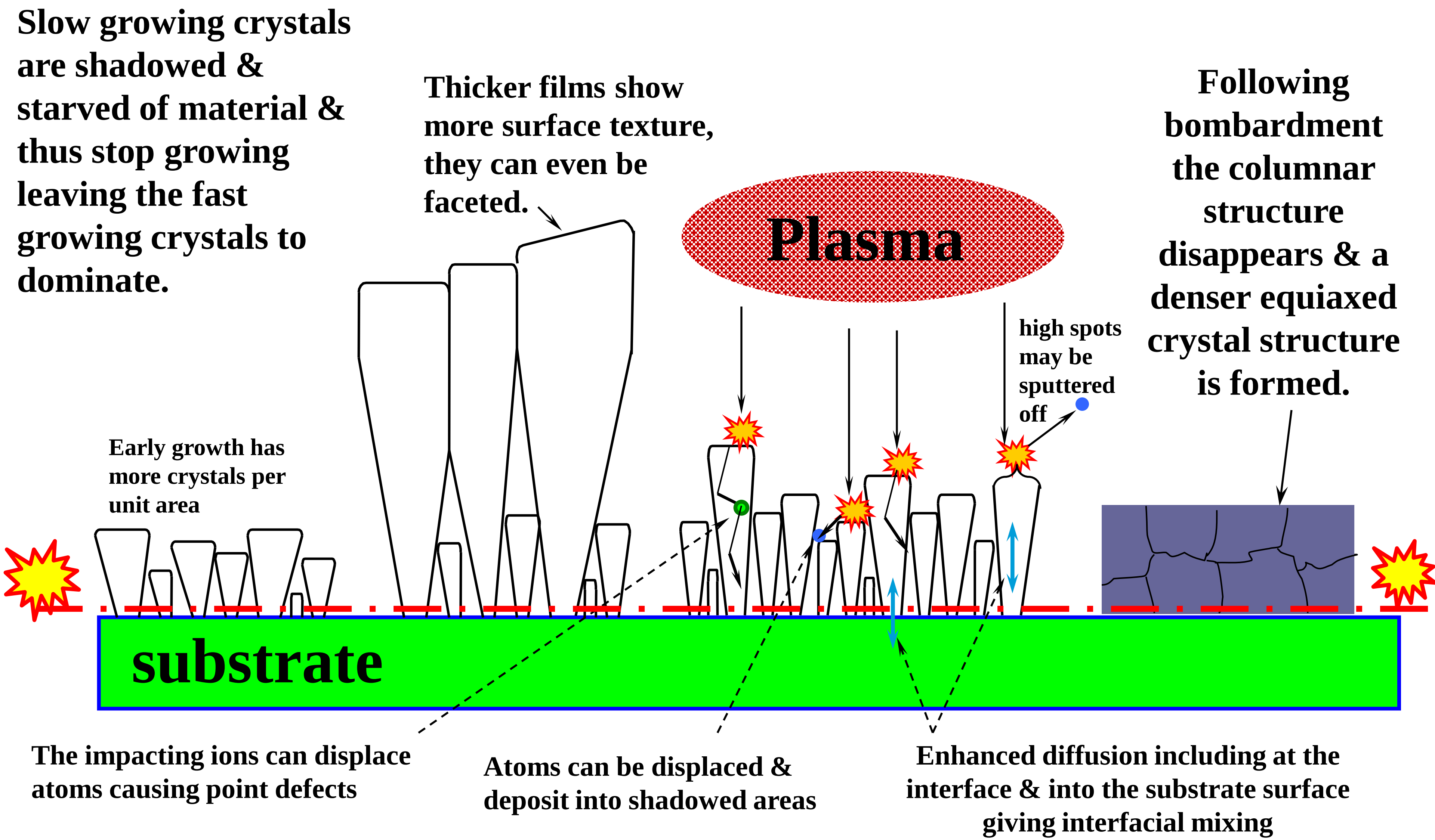


500,000 x magnification

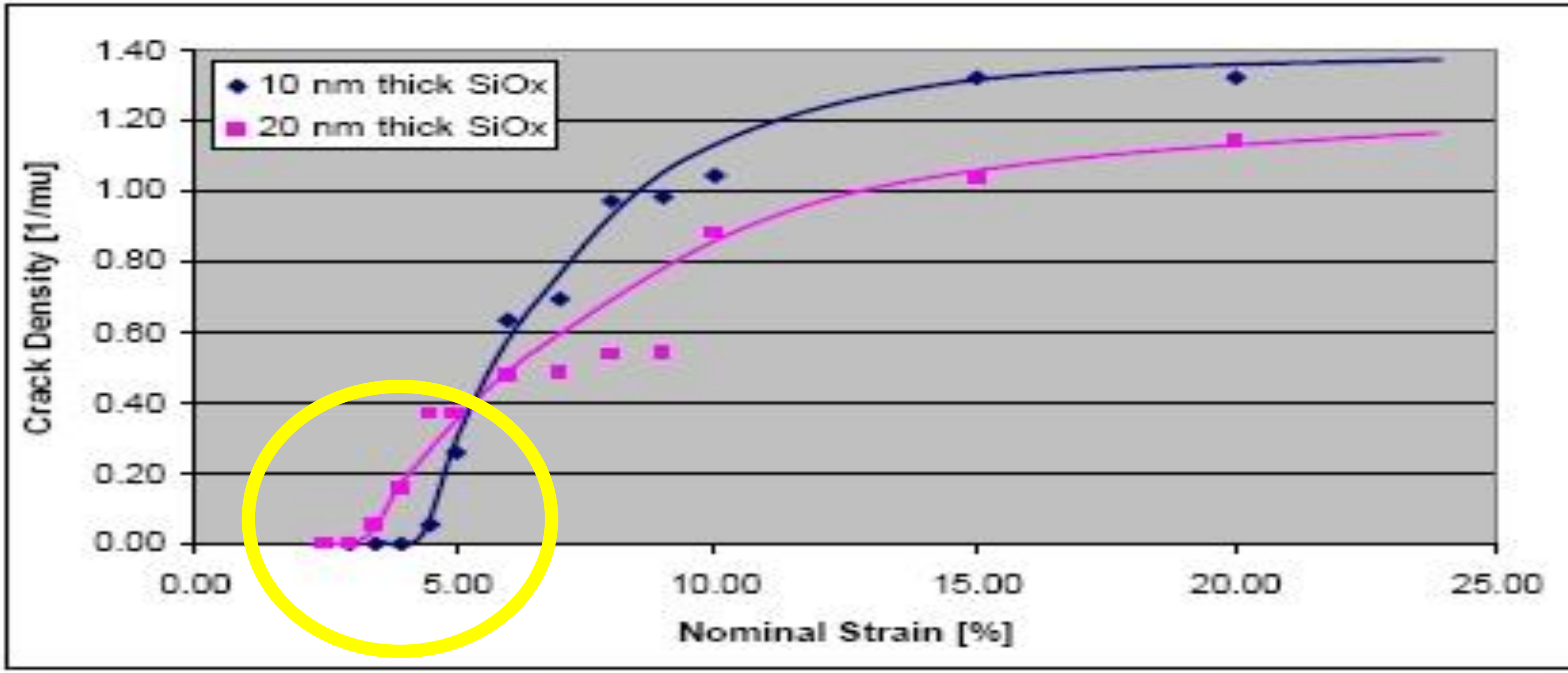


In reality the coatings can be quite thick but still contain defects or holes that reach the substrate. High surface energy & good wetting help minimise this

Microstructure modification



Onset of cracking



Sample	SiOx thickness [nm]	Crack Onset Strain [%]
SiOx / PET (RDO12)	20	3.5
	10	4.5

Materials

Polymers / organic materials

Substrates

- Polyester (PET,PEN)
- Polypropylene (PP, OPP,CPP)
- Polyethylene, (PE, LDPE, HDPE, Linear LDPE, ULDPE….)
- Polyamide (Nylon)
- Biopolymers
- Others
  - Cyclic Oxalic Copolymers (COCs)
  - Liquid Crystal Polymers (LCPs)
  - Polycarbonate (PC)

Coatings

- Ethylene vinyl alcohol (EVOH) - Polyvinyl alcohol (PVOH)
- Poly vinyl dichloride (PVdC) – (banned in some countries)
- Adhesives (heat seal, lamination, polyurethanes, polyethylene…)
- Acrylates (inc. in-vacuum coatings)

Inorganic coatings

Compounds

- Silica, silicates
- Alumina
- Metal oxides – ITO, SnO, ZnO, etc
- Metal nitrides
- Metal oxynitrides
- Metal carbides, oxycarbides, etc
- Graded compounds

Metals

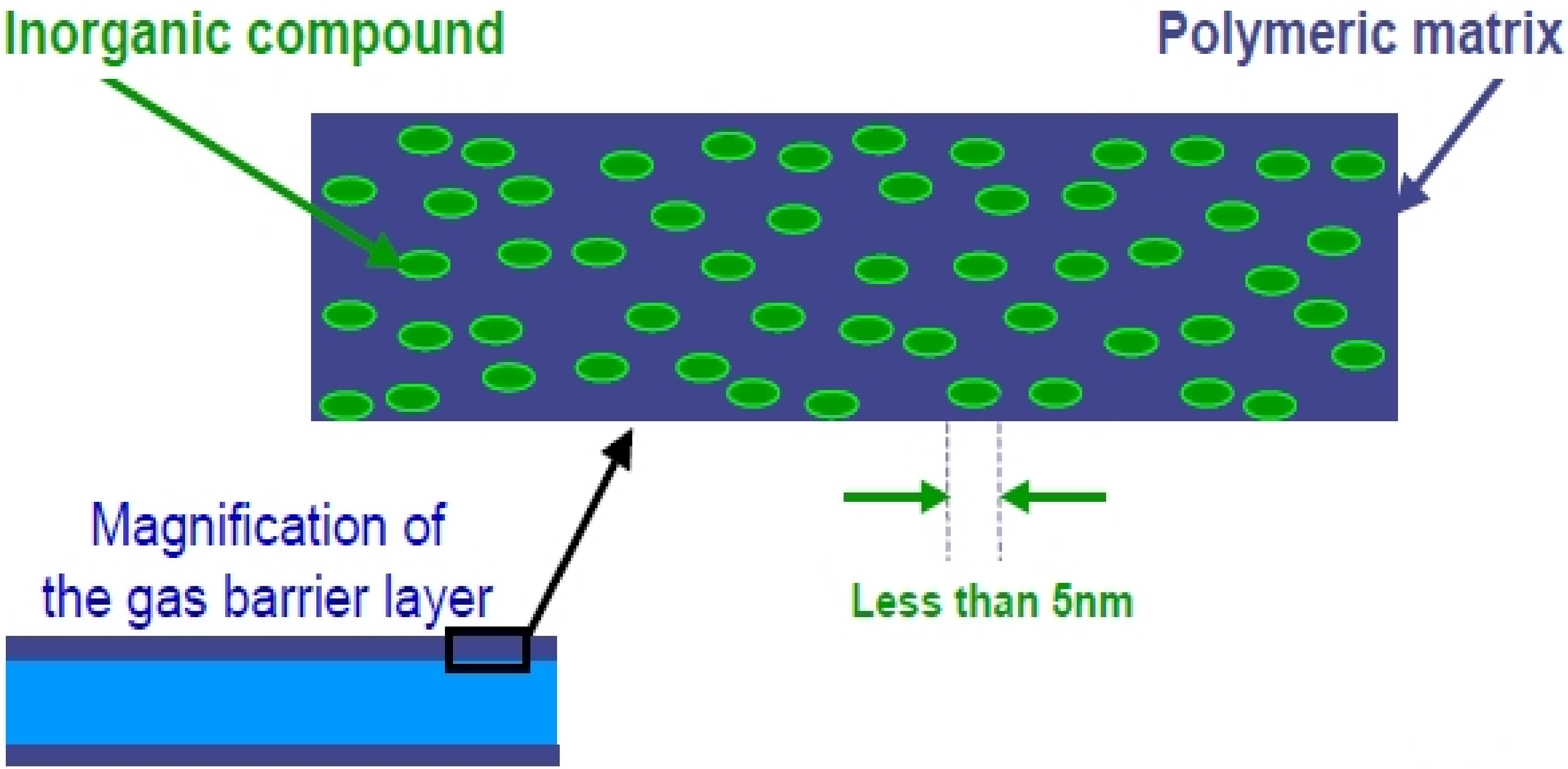
- Aluminium

Others

- Carbon
- Melamine (1,3,5-triazine-2,4,6-triamine)

Kuraray's technology at work

- An inorganic compound is dispersed in a polymeric matrix, to create a tortuous path for gas molecules (long gas diffusion path).
- Molecular movement of the polymer chain is restricted by the inorganic compound (low gas diffusion rate).

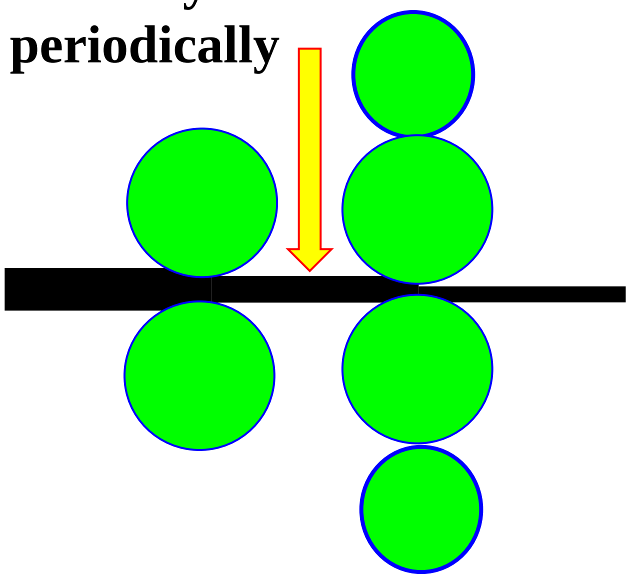


Barrier Material	Thickness	Oxygen Transmission [ccm/m2/day/atm]	Water Vapour Transmission [g/m2/day/atm]	Deposition Process	Coating type	Relative cost
PET / Blank	12.00 μm	100	64.64			1x
PVDC	24.00 μm	8	0.3			
EVOH	24.00 μm	0.16 - 1.86 *	N/A			3x
m-OPA	15.00 μm	30				
Aluminized PET (single)	~ 30nm	0.31 - 1.55	0.31 - 1.55	Evaporation	Al	2x
Aluminized PET (double)	~ 30nm each	0.03	N/A	Evaporation	Al	~3x
Aluminium on PE	7μm Al	0.001	N/A	Laminated	Al	
SiOx on PET	10 - 80 nm	0.35 - 10**	0.46 - 1.24	Evaporation	SiOx	3x
SiOx on PET or SiOx containing Carbon	10 - 80 nm	0.08 - 1.55	0.5 - 5.0	PECVD	SiOx or Si(C)Ox	3x
Al2O3 on PET	20 nm	1.5	5	Evaporation, or Reactive Evaporation	Al_2O_3	2.25x - 2.5x
Al_2O_3/SiO_x on PET	50 nm	2.0 - 3.0	1	Evaporation	Al_2O_3/SiO_x	2.5x - 3x
Al2O3 on PET	<5 nm	~1.5 (improving 0.0001 claimed)	~5 (improving 0.0001 claimed)	ALD - Atomic Layer Deposition	Al_2O_3	aim to be < 2x
Diamond-like Carbon on PET	20 nm	2	1.5	PECVD	Carbon (DLC)	2.5x - 3x
Melamine on PET	12.00 + 0.25μm	<5		PVD	Triazine	2.5x - 3x
Melamine on OPP	20.00 + 0.25 μm	30		PVD	Triazine	2.5x - 3x
OPP / Blank	20.00 μm	1600				

- * depending on relative humidity and ethylene content
- ** depending on process

Foil

Foil may be annealed periodically

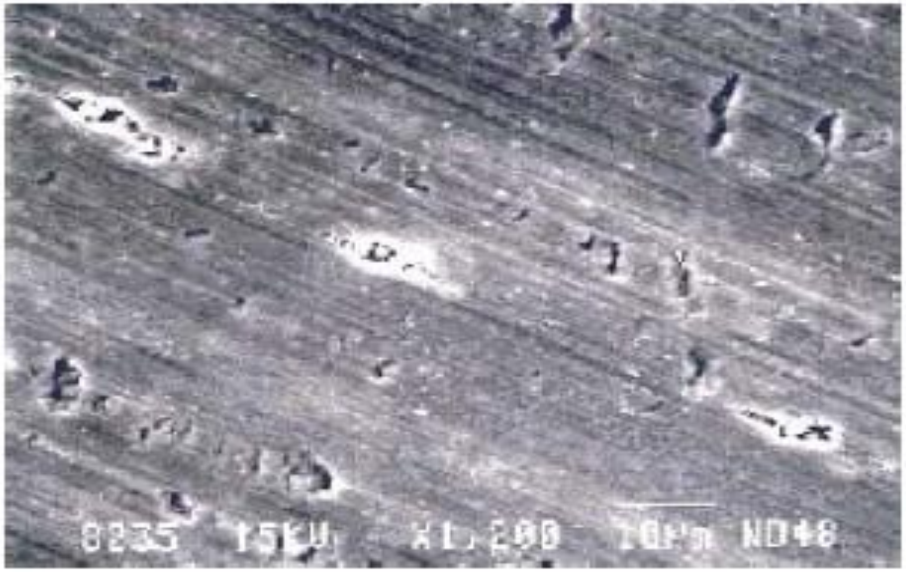


foil - 2.2m wide 2,500 m/min
6 microns thick

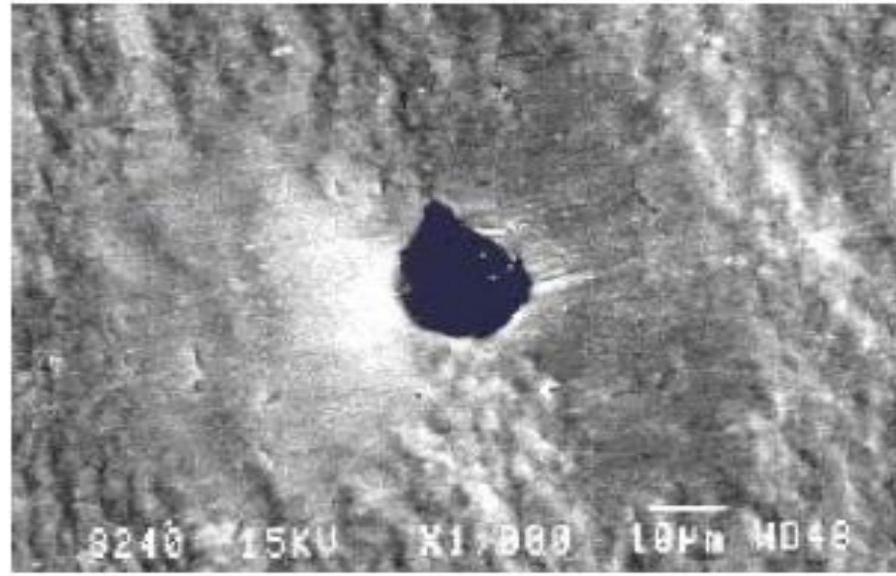
Maximum Allowable Pinhole Count in One Square Meter

Foil Gauge	Foil Caliper, μ	Average	Maximum
28.5	7	423	1584
35	9	211	1056
50	13	85	528
75	18	21	106
100	25	0	0

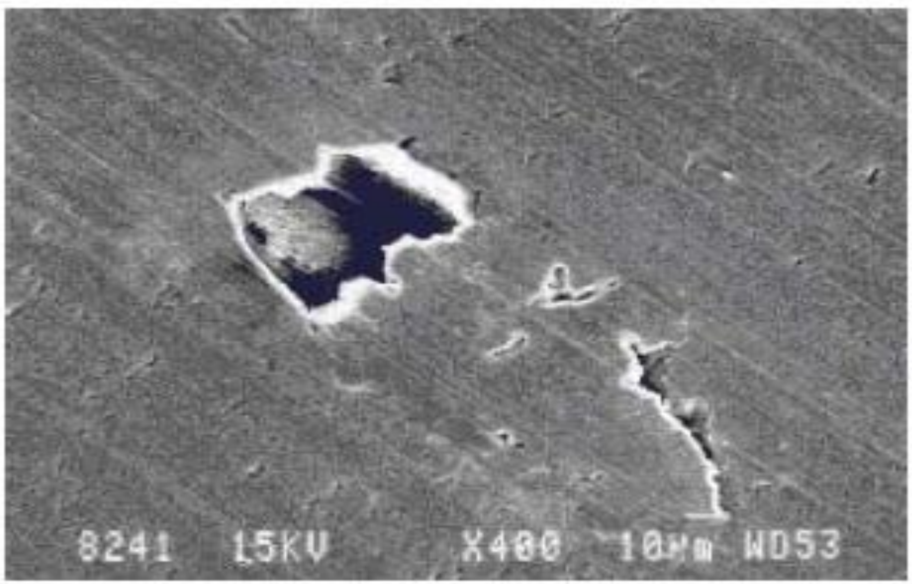
Examples of Typical Foil Pinholes



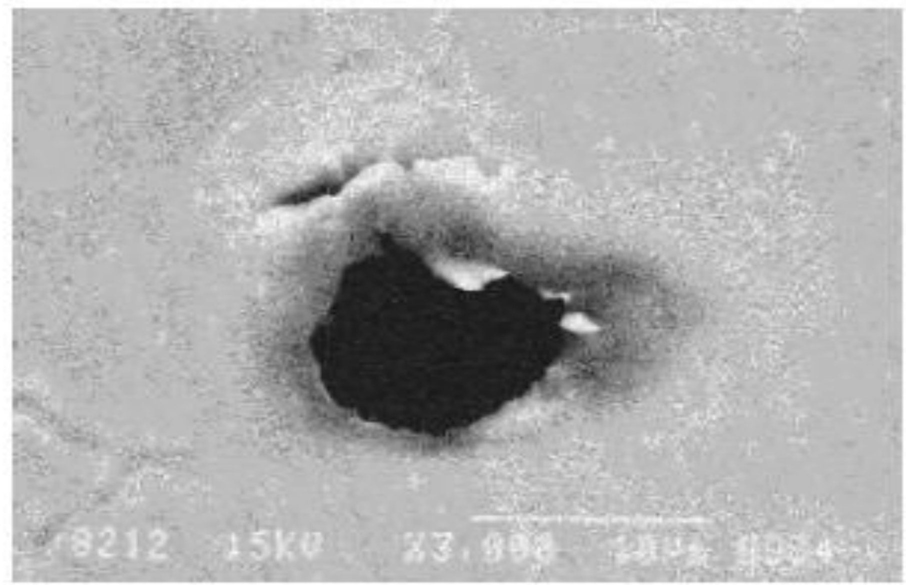
Pinholes from Al-Fe-Si Constituents



Pinhole from Depression in Foil

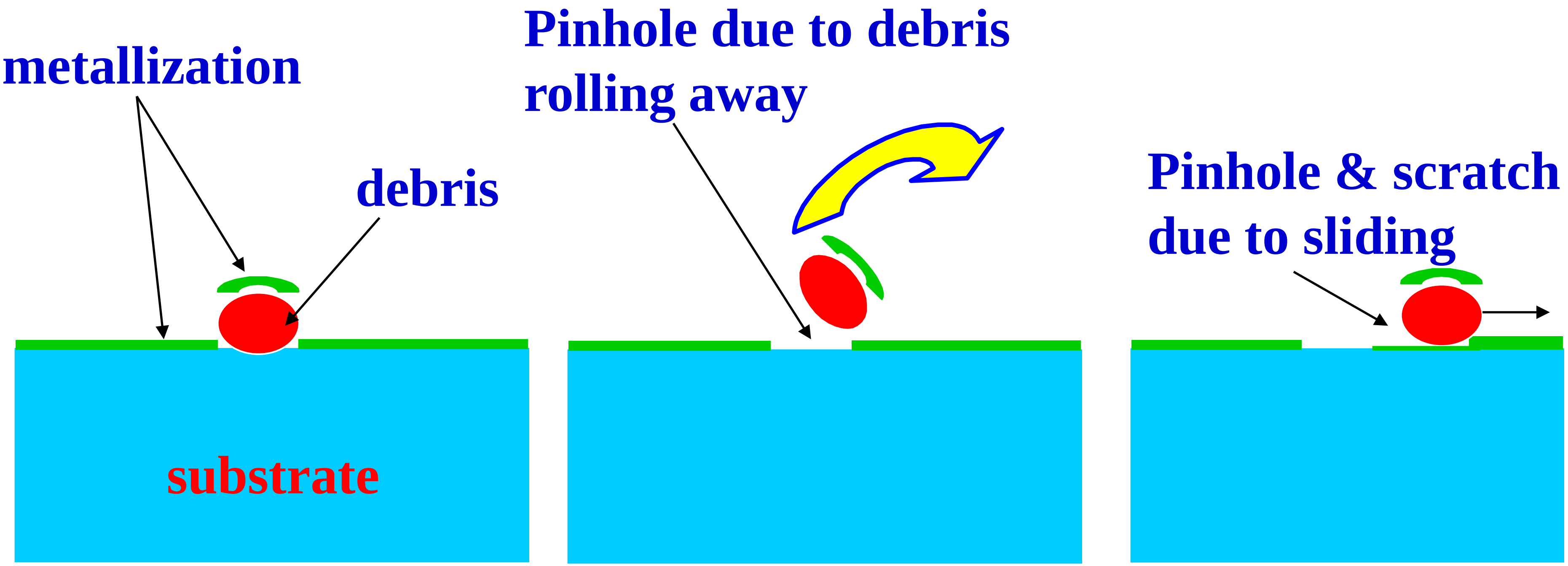


Pinhole from rolling Debris



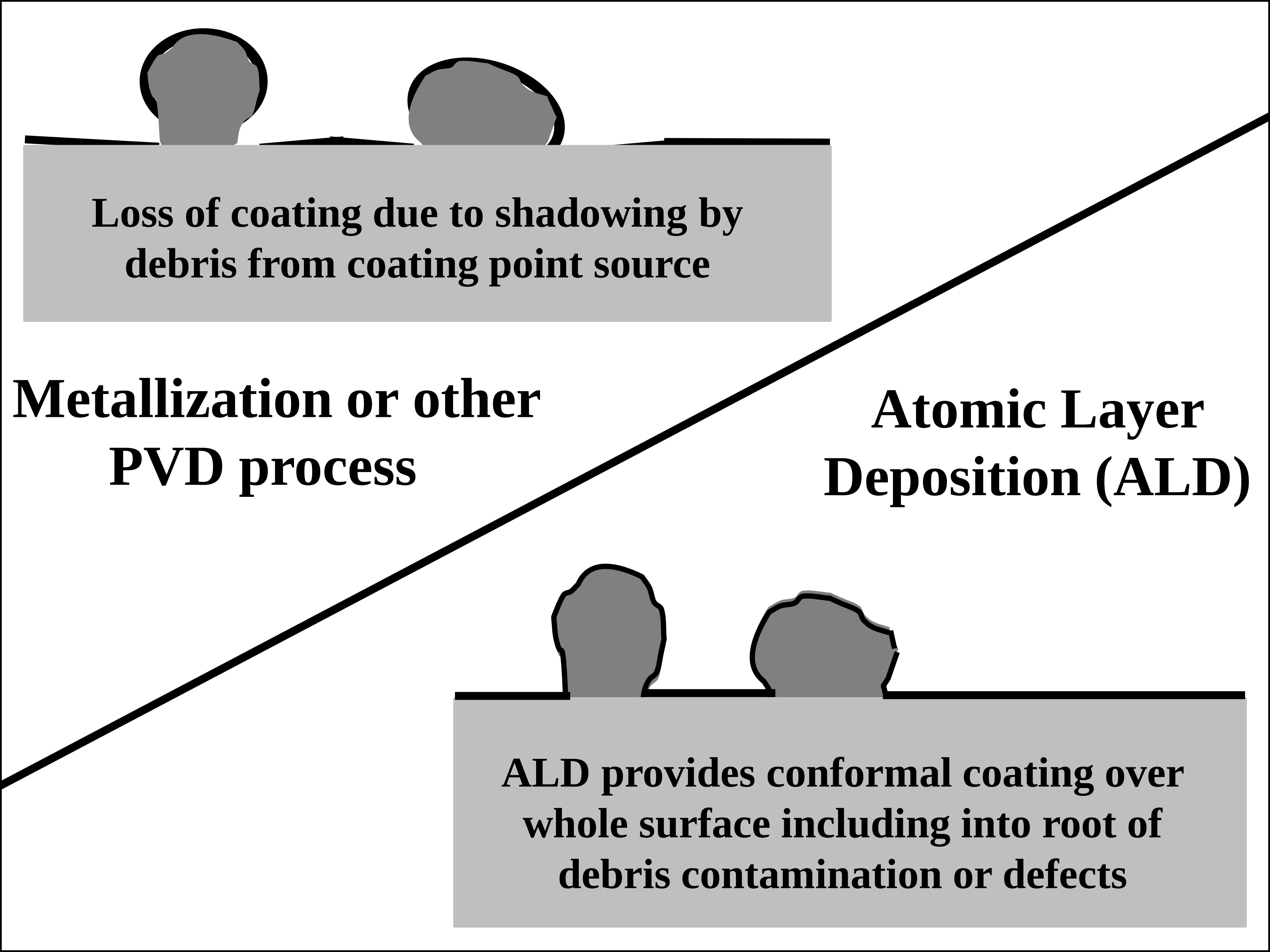
Pinhole from Aluminum Fines Damage

Pinholes

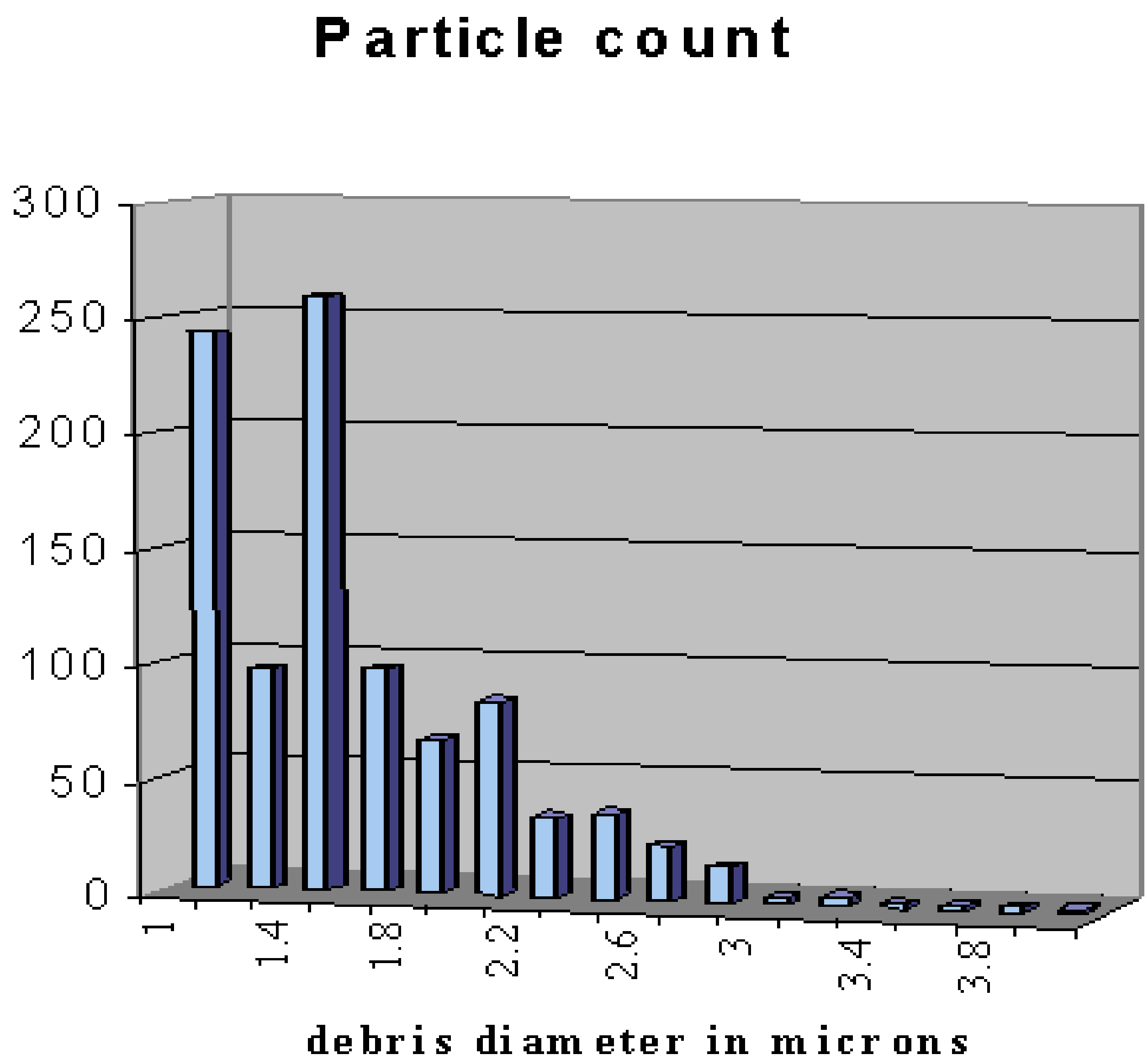


Debris typically >0.5 microns

metalized layer 20 – 100nm


Loss of coating due to shadowing by
debris from coating point source
Metallization or other
PVD process
Atomic Layer
Deposition (ALD)
ALD provides conformal coating over
whole surface including into root of
debris contamination or defects

Surface defects

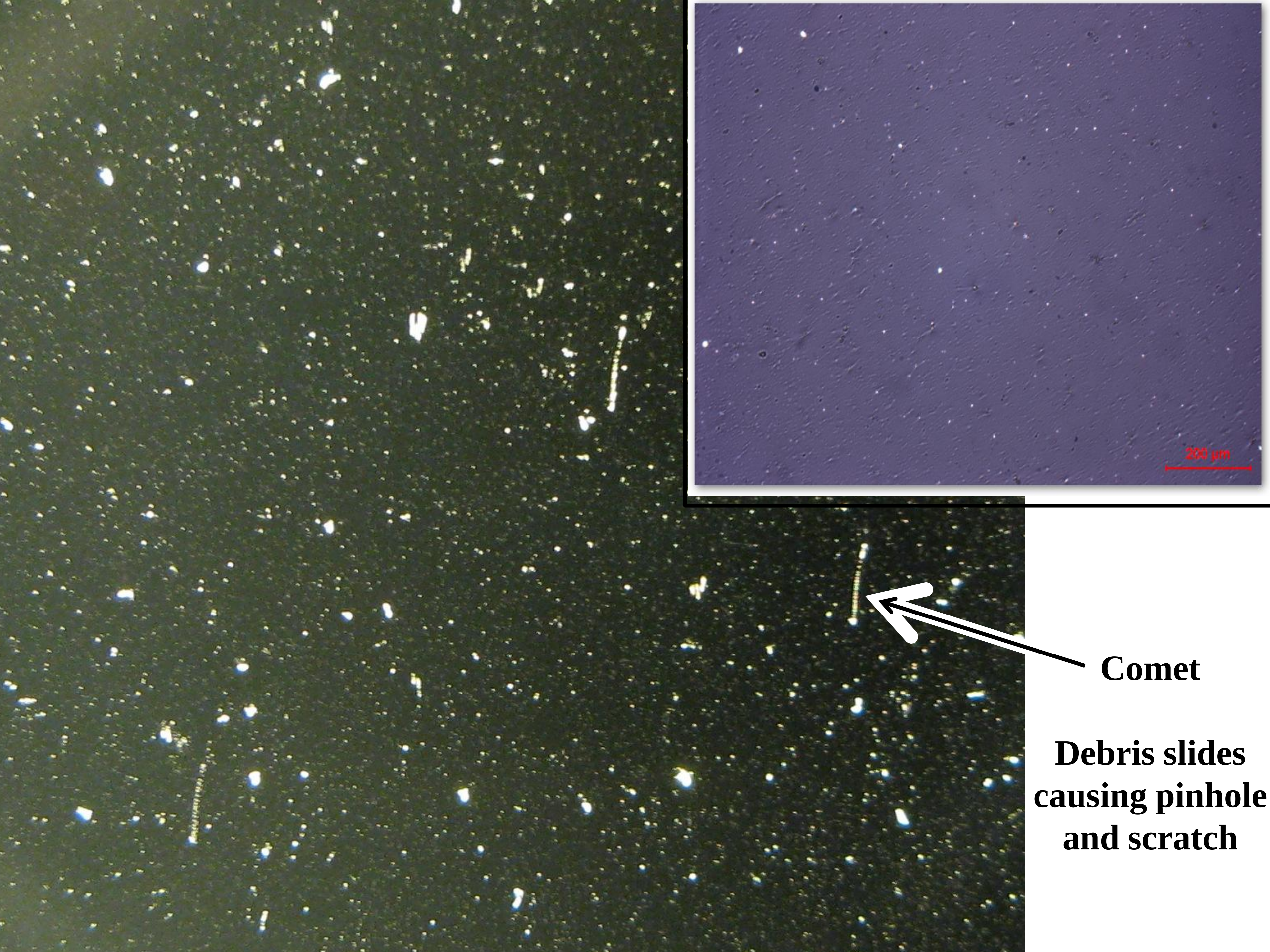


Incident Dark Field
Optical Microscopy
Or
Differential Interference
Contrast Microscopy

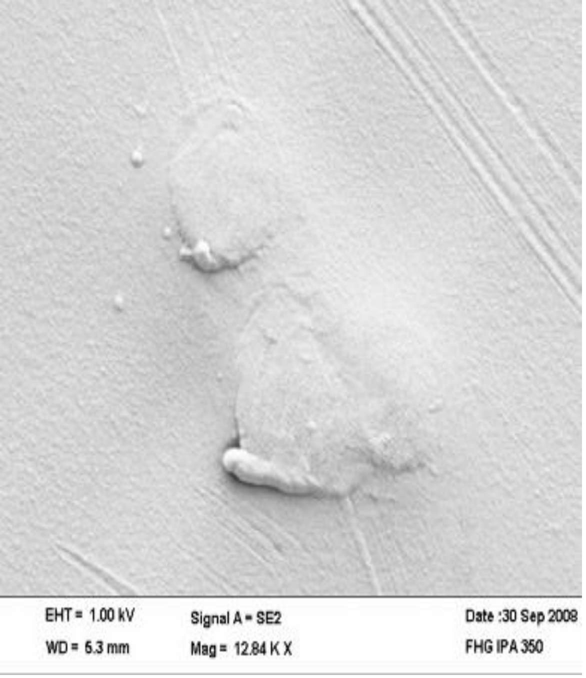
Area used for the analysis was 170 x 170 microns

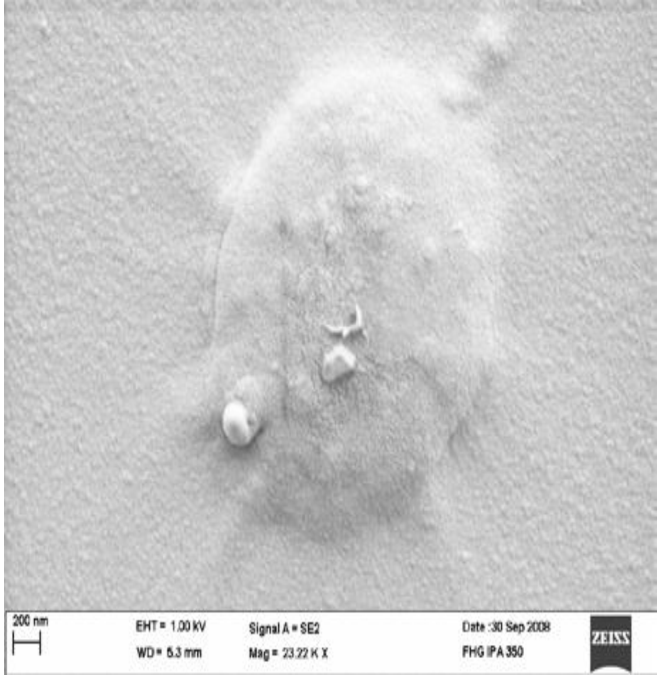
Magnification 400x.

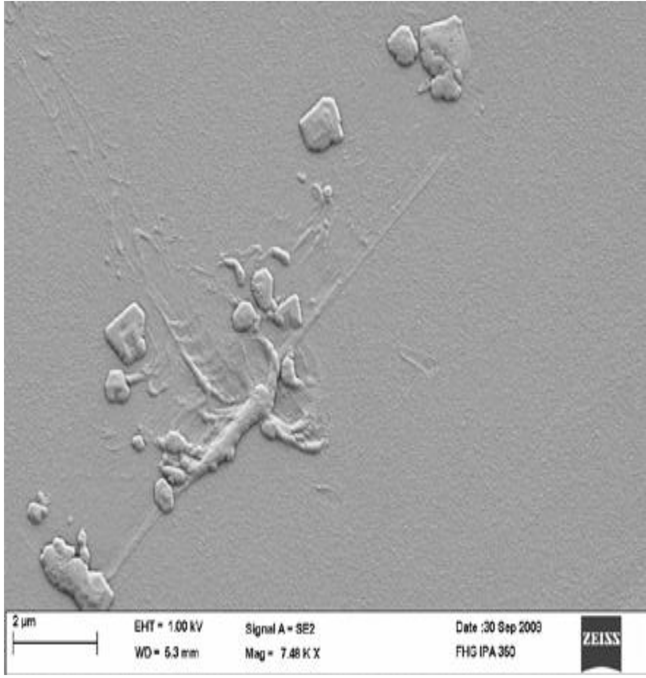
Average of 6 different fields of view

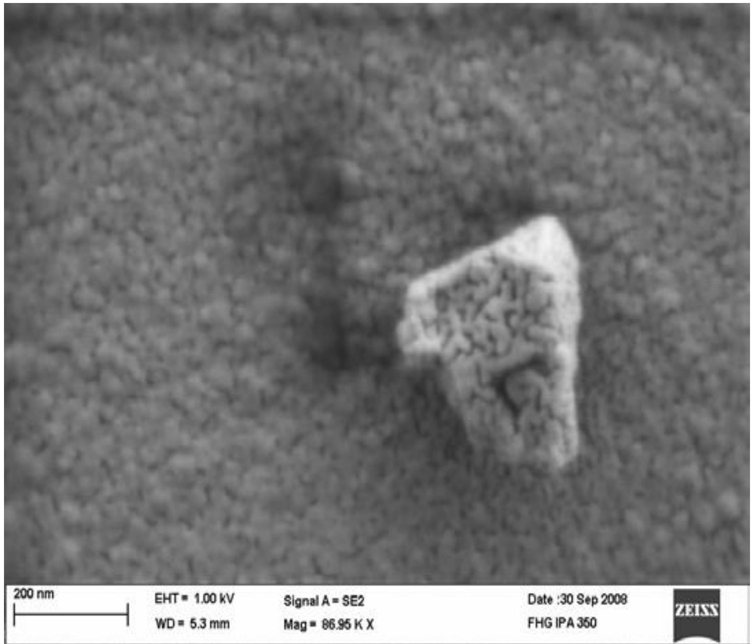

200 µm
Comet
Debris slides causing pinhole and scratch

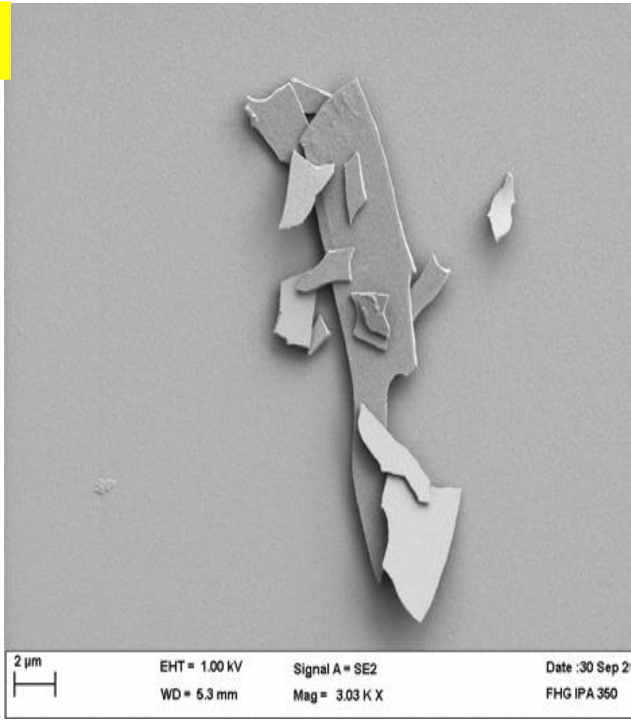
SEM of defects – FEP IVV Freising



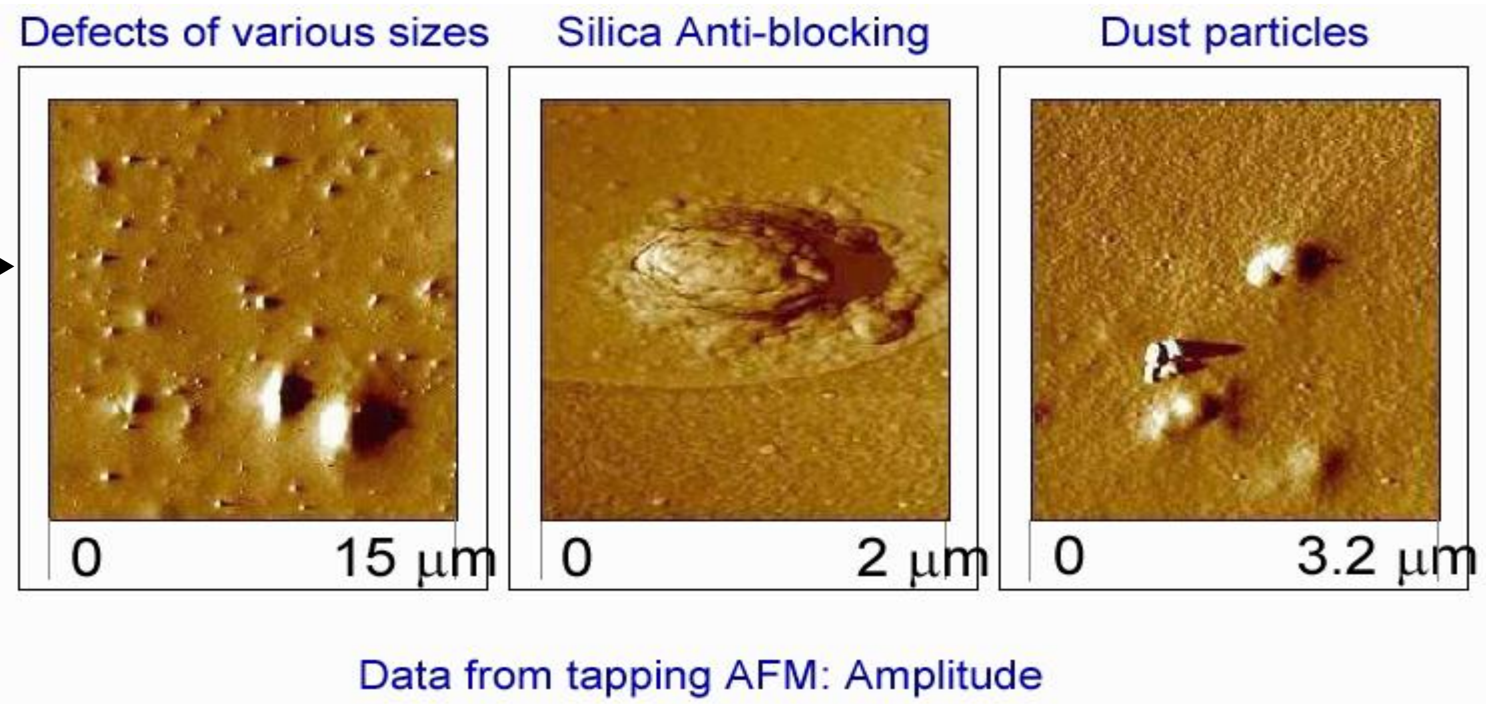


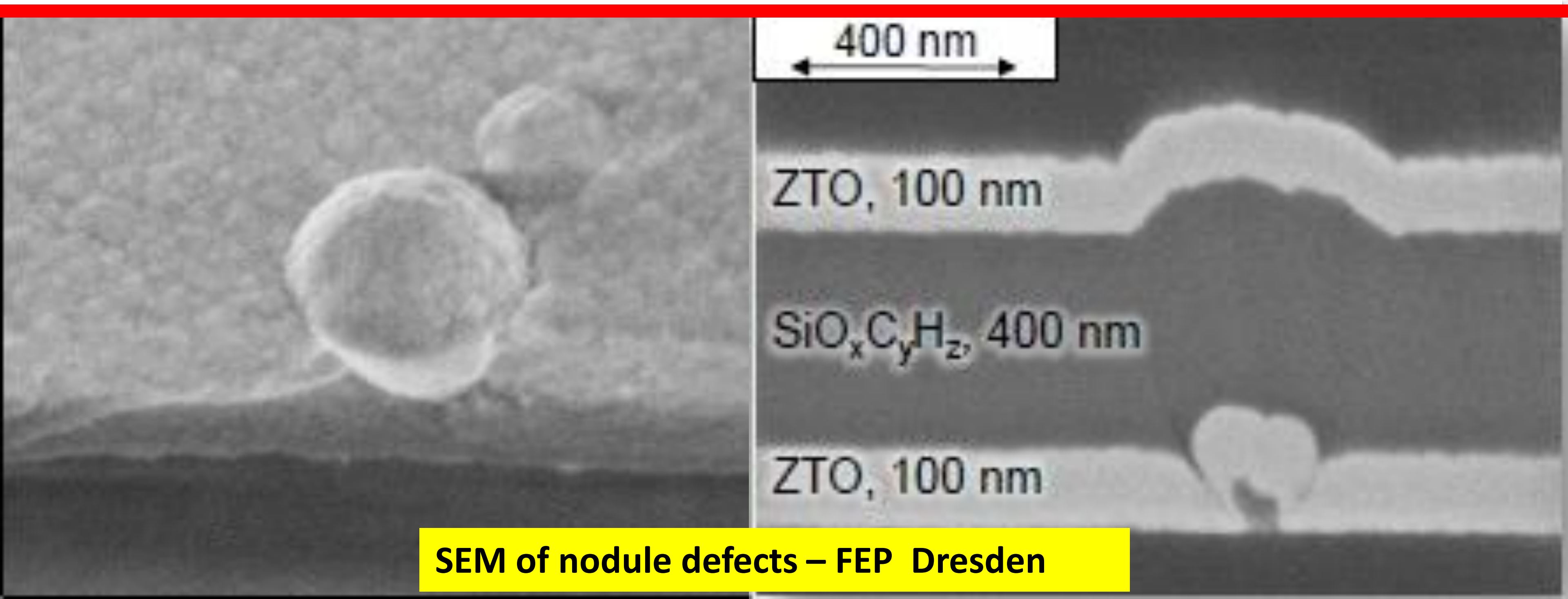






Images courtesy of TetraPak





SEM of nodule defects – FEP Dresden

Source of debris

People emit a very large number of particles

standing still humans emit 100,000 particles per minute (ppm)
standing up from a sitting position humans emit 2,500,000 ppm
(definition of a particle is debris of 0.5 microns or larger)

This comprises hair, skin and micro-salt crystals
skin in the range 0.1 – 5 microns   Hair in the range 5 – 100 microns

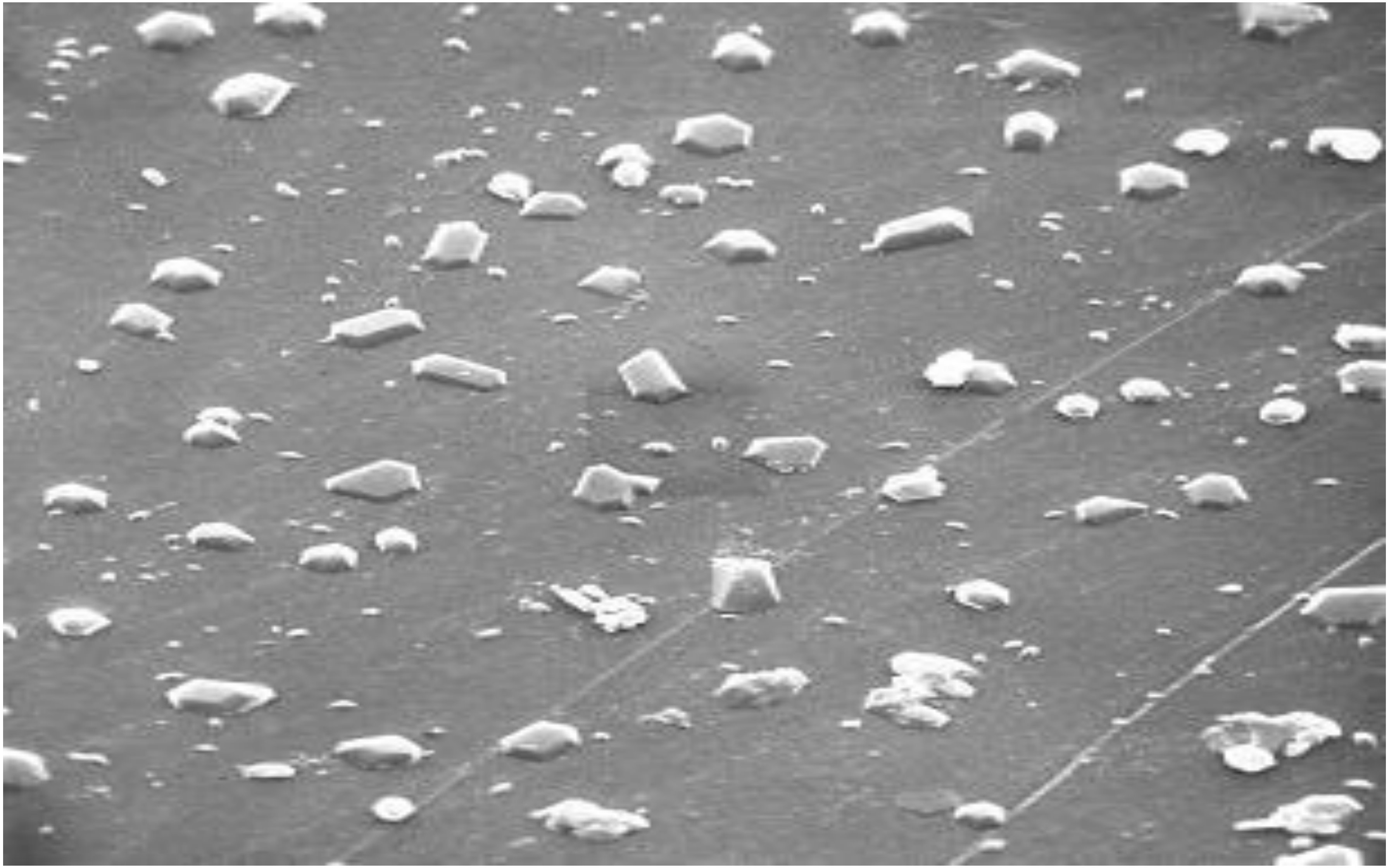
<u>Resolution of eye</u>

A working value ~50 microns
(quoted range 10 – 100 microns)

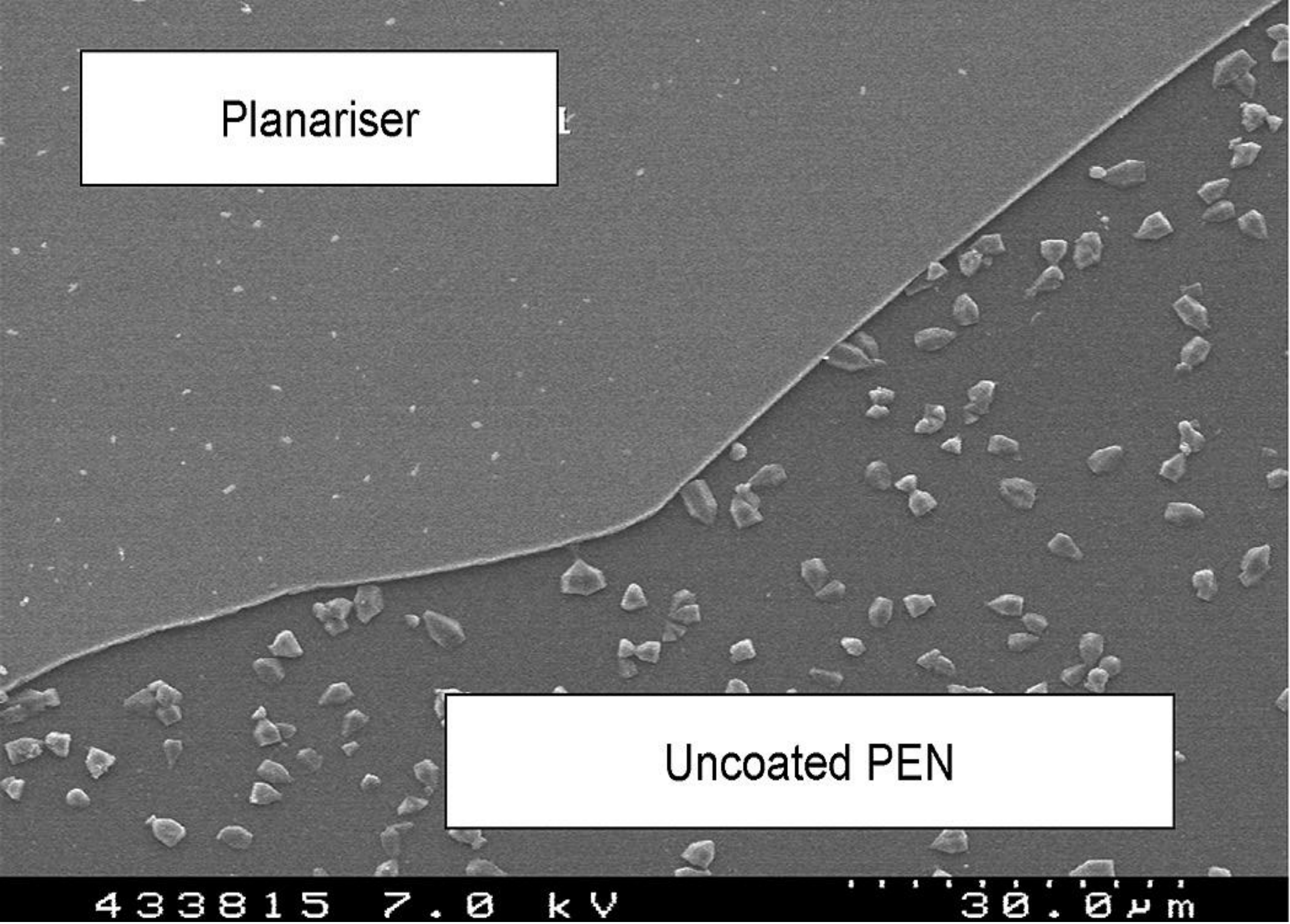
<u>Practical example</u>
Human inspection expected to resolve 50% of 50 microns debris on a surface

Activity generating particles	microns
Pollens	10 - 100
Rubbing ordinary painted surface	90
Sliding metal surfaces (unlubricated)	50 to 150
Crumbling or folding paper	60
Rubbing epoxy painted surfaces	30 to 75
Seating and unseating screws	25 to 120
Belt drive	5 to 35
Writing with ballpoint pen on paper	15 to 30

Oligomer growth

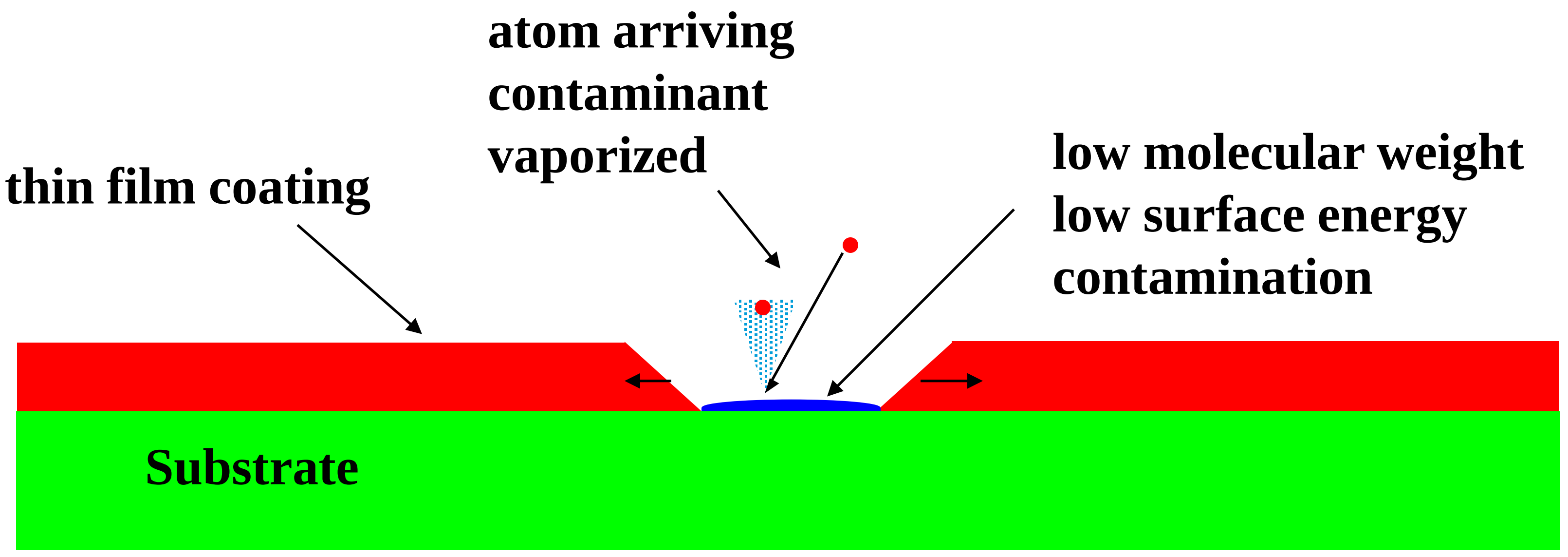


PET (442) after prolonged heating 1hr @ 140 Deg C SEM at 2000x magnification
Showing growth of 'mer' units into dimers, trimers, etc



Source: Bill MacDonald DuPont Teijin Films J. SID 15/12, 2007 p1075

Reticulation pinholes



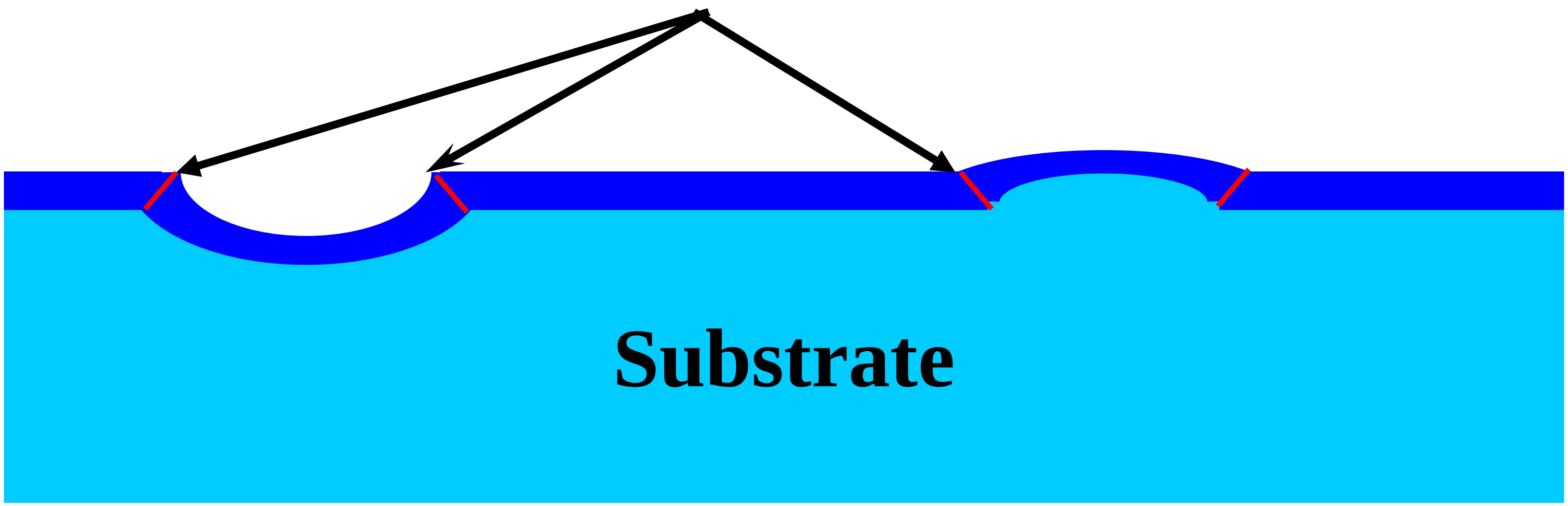
The atoms nucleate on the higher surface energy part of the substrate but not on the low molecular weight contamination

Low molecular weight contamination can be vaporized by depositing atoms preventing any deposition. This low molecular weight material may be oligomer

Stress raisers

Surface defects i.e. dents or bumps lead to defects in the coatings

The coating thinner over the defect (> surface area for same coating thickness) & also the edges of the defect are prone to cracking



Cleaning options

Options for cleaning polymer film surfaces

- Cloth wipe
- Static brush
- Rotating brush

Surface contact can cause damage

- Air blower / knife
- Vacuum cleaner

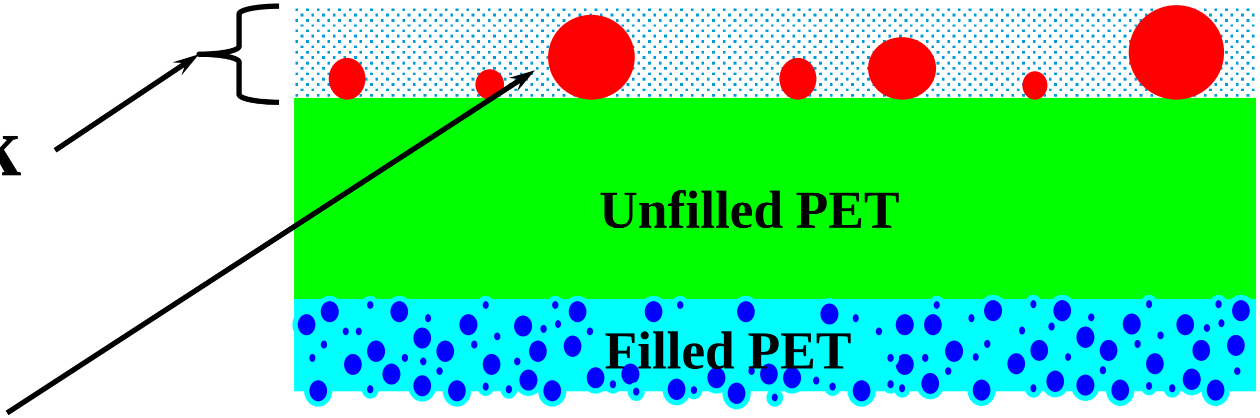
Difficult to breakthrough entrained air

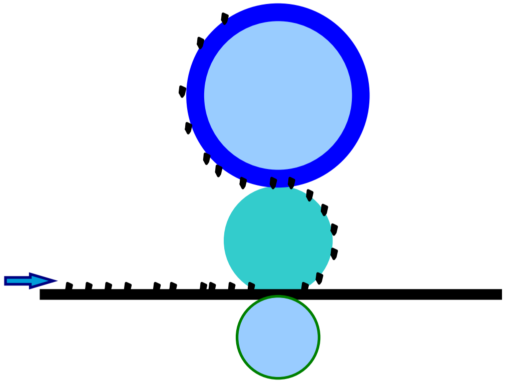
- Electrostatic neutralised ultrasonic pulsed air jet & vacuum extract
- Transfer tack rolls
- Planarization and/or Overcoating (best combined with pre-cleaning first)
- Carbon Dioxide ‘snow jet’

Polymer pre-layer

No cleaning requires thick coating

Large debris





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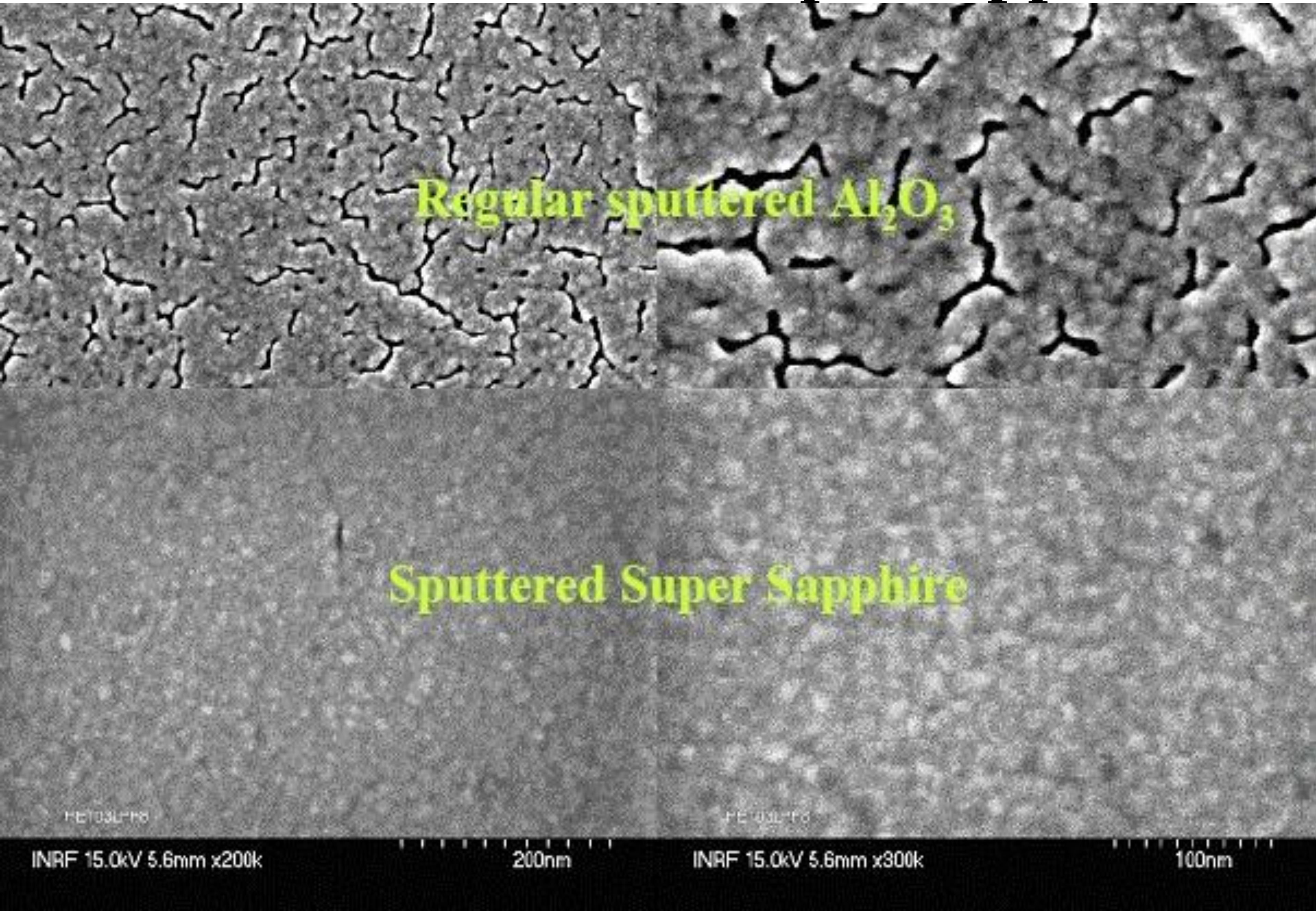
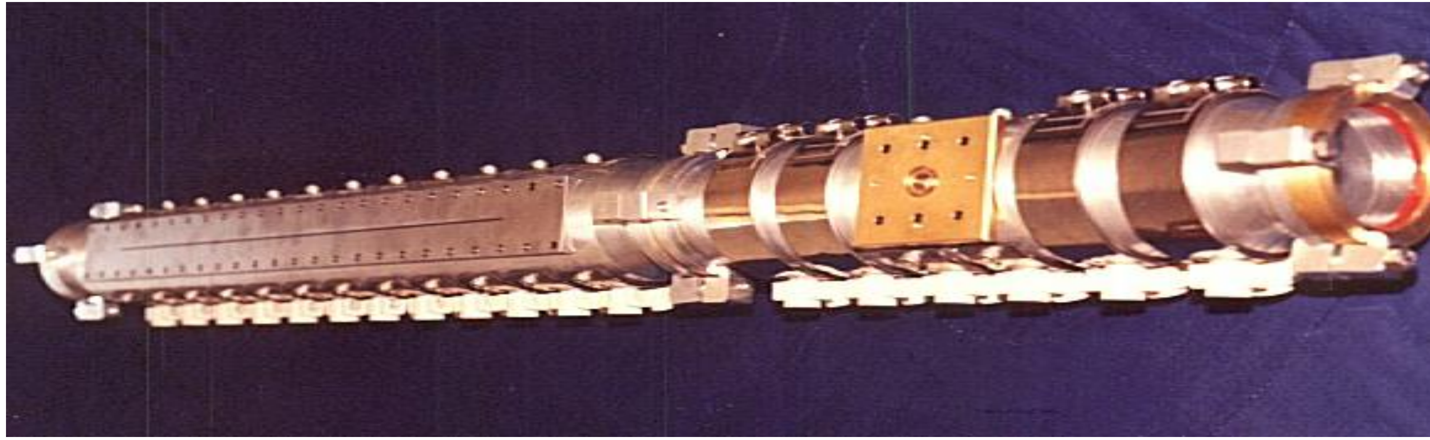
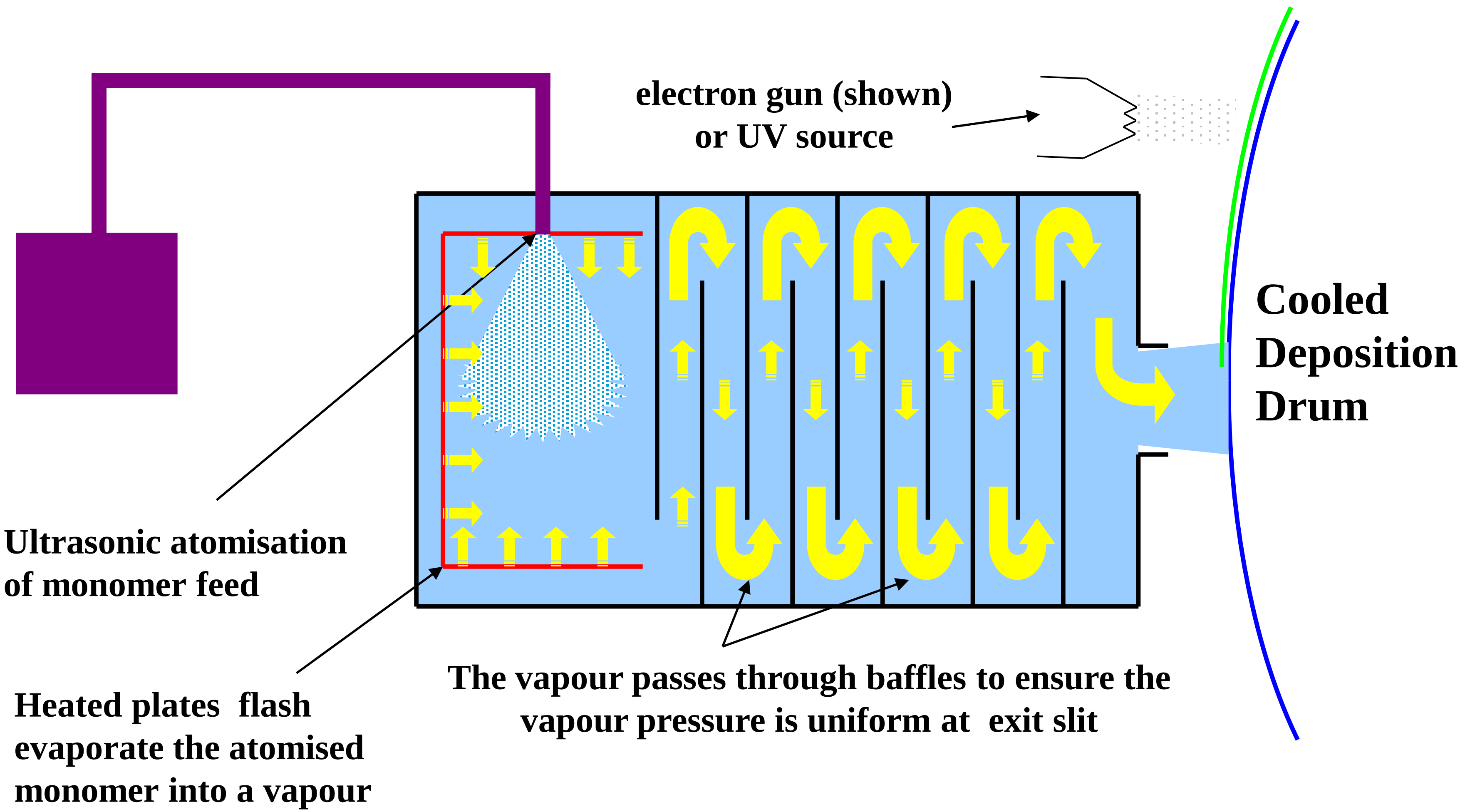
Cleaning = fewer, smaller debris & thinner coating

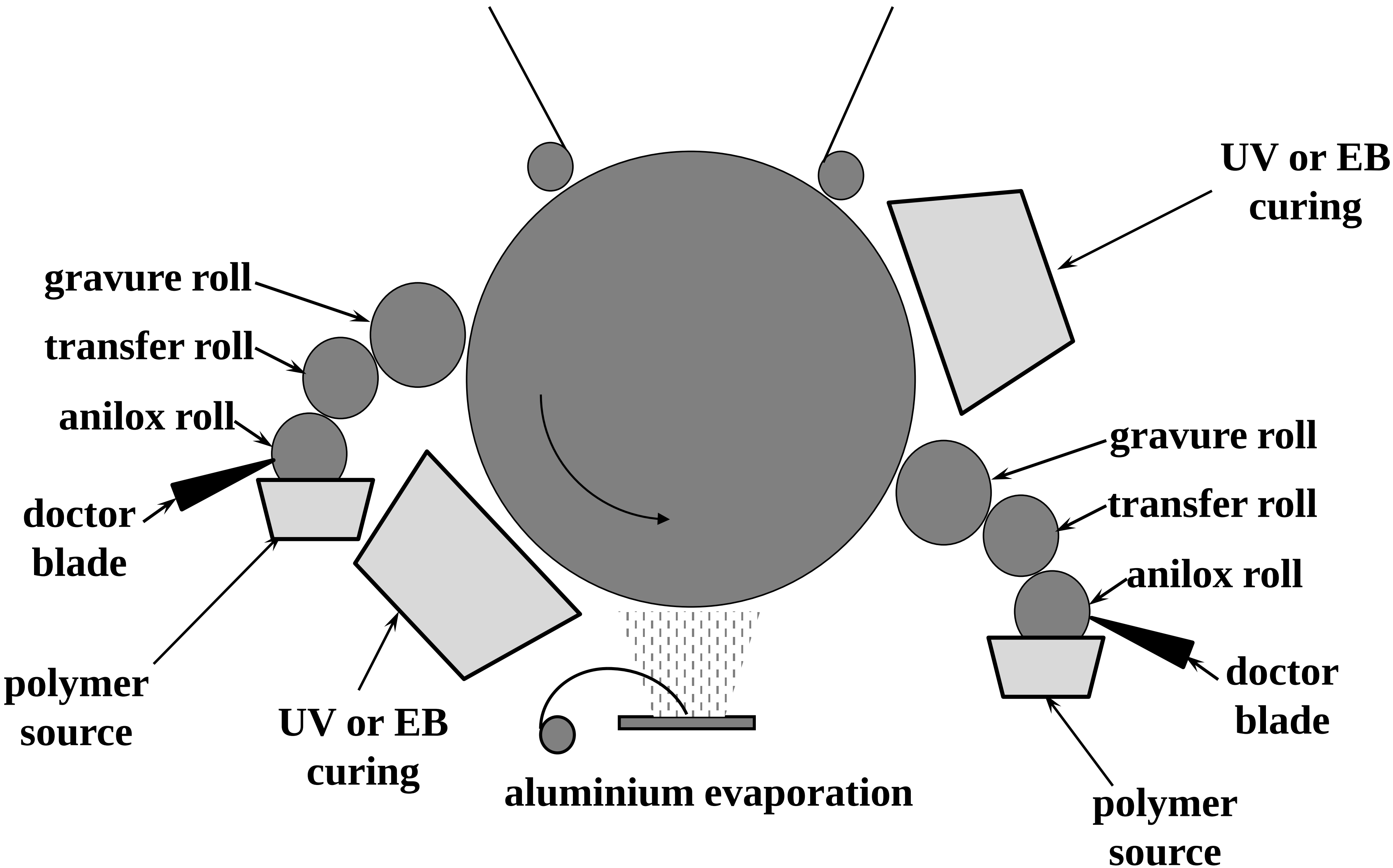
General Atomics – Super sapphire





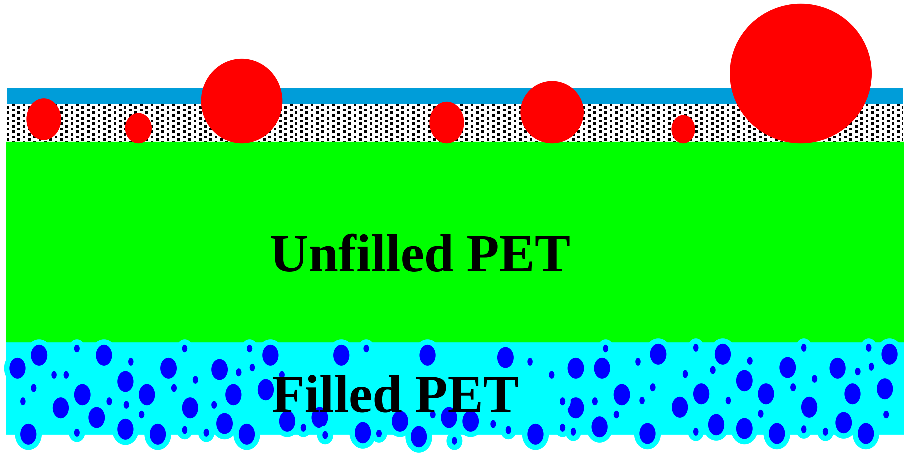

electron gun (shown)
or UV source
Cooled
Deposition
Drum
Ultrasonic atomisation
of monomer feed
Heated plates flash
evaporate the atomised
monomer into a vapour
The vapour passes through baffles to ensure the
vapour pressure is uniform at exit slit

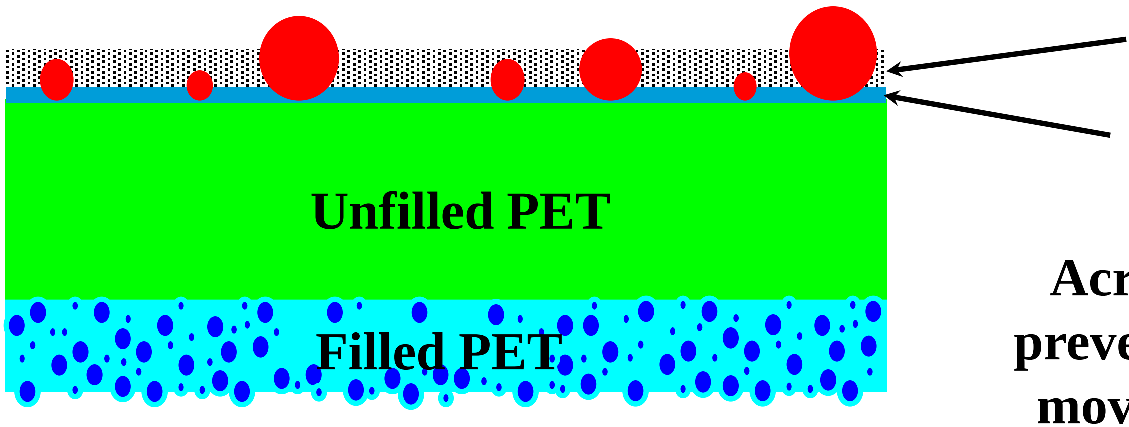
Pre / Post Acrylate Monomer Printing



Polymer layers

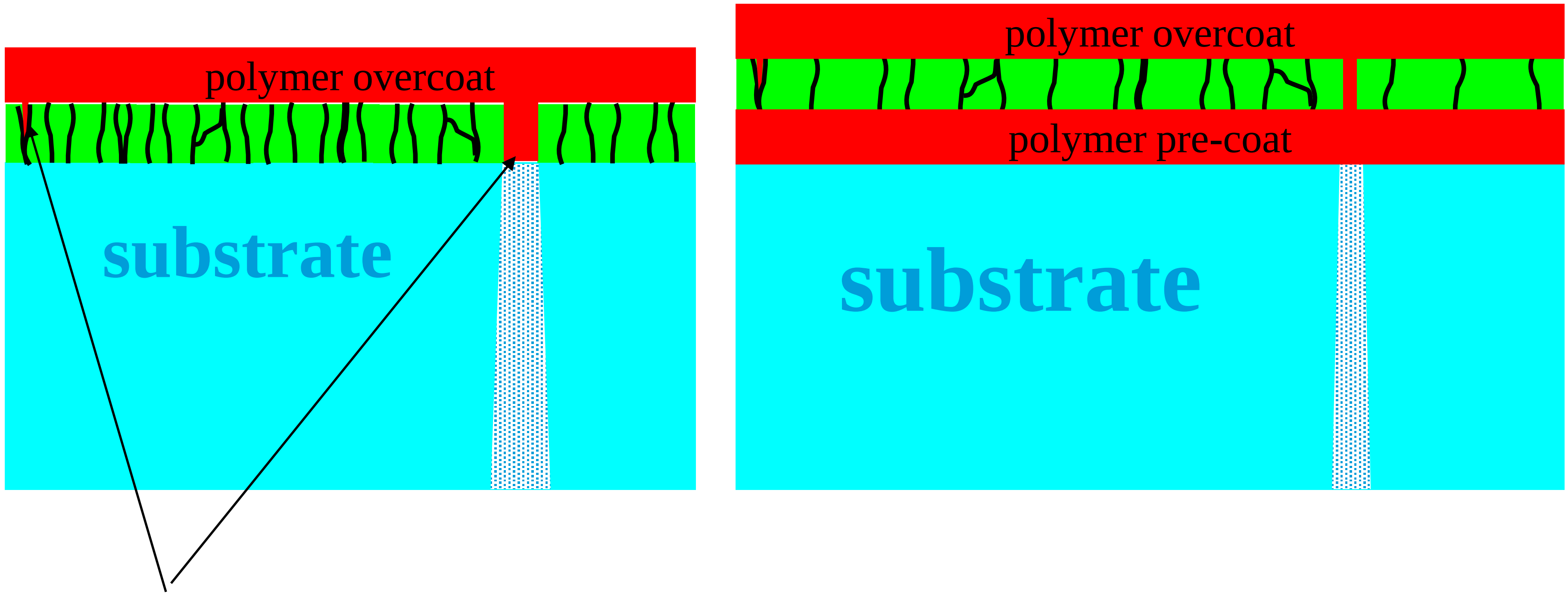
Sigma International - Benefits of polymer layers.	
Materials	No.pinholes/unit area
OPP + Al	1760
OPP + Polymer + Al	590
OPP + Al + Polymer	35





Acrylate hides some debris & prevents some others from being moved. If debris is moved the polymer protects the metal coating

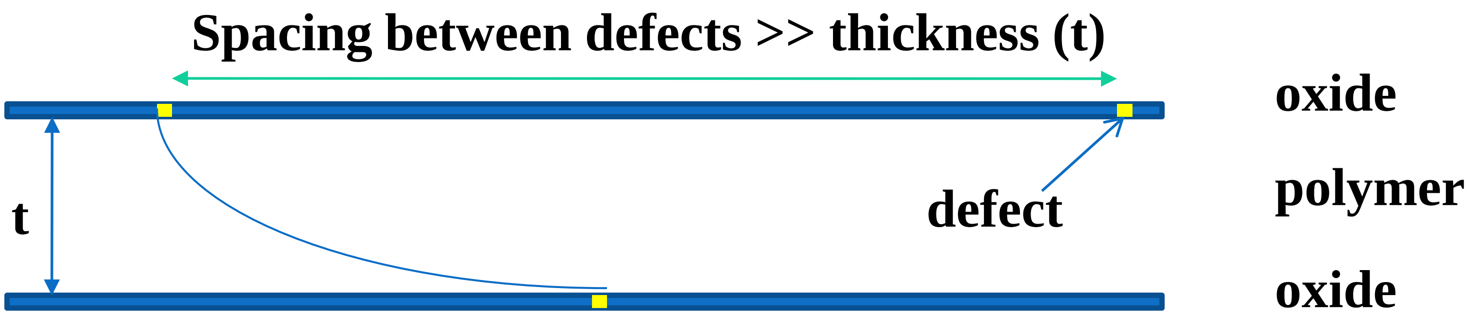
Defects



The polymer is drawn by capillary action into pores thus partially sealing them. Adding a nano-flake further improves the diffusion coefficient of the coatings. Ideally the flake size is small enough to fill and plug any cracks, pores or pinholes in the coating.

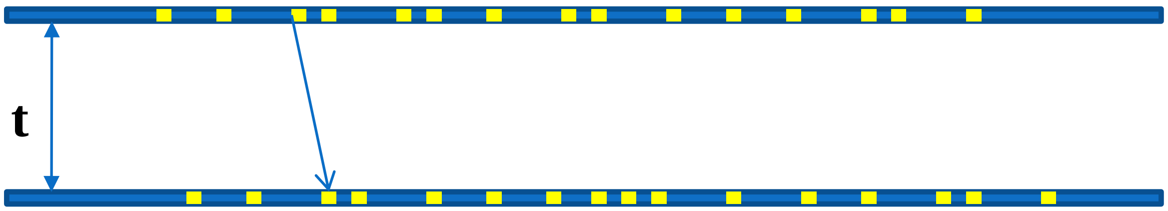
Barrier performance

Aluminised PET (single)	~ 30nm	0.31 - 1.55	0.31 - 1.55	Evaporation	Al
Aluminised PET (double)	~ 30nm each	0.03	N/A	Evaporation	Al

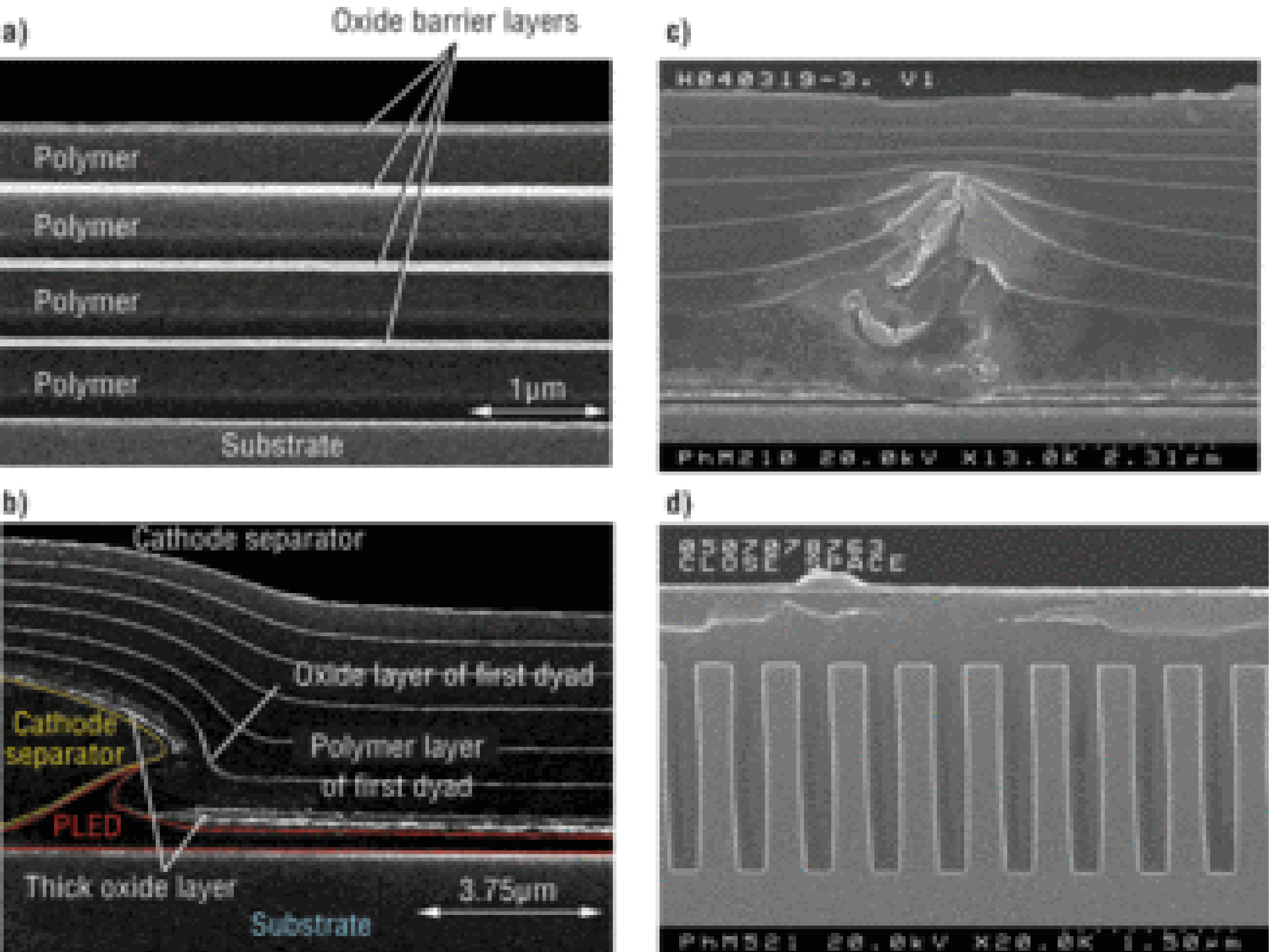


When the defect spacing is large compared to the thickness the diffusion path becomes very long as shown above

By comparison a greater density of defects results in the diffusion distance being ~ = equal to the polymer thickness



Polymer / oxide barriers - Barix



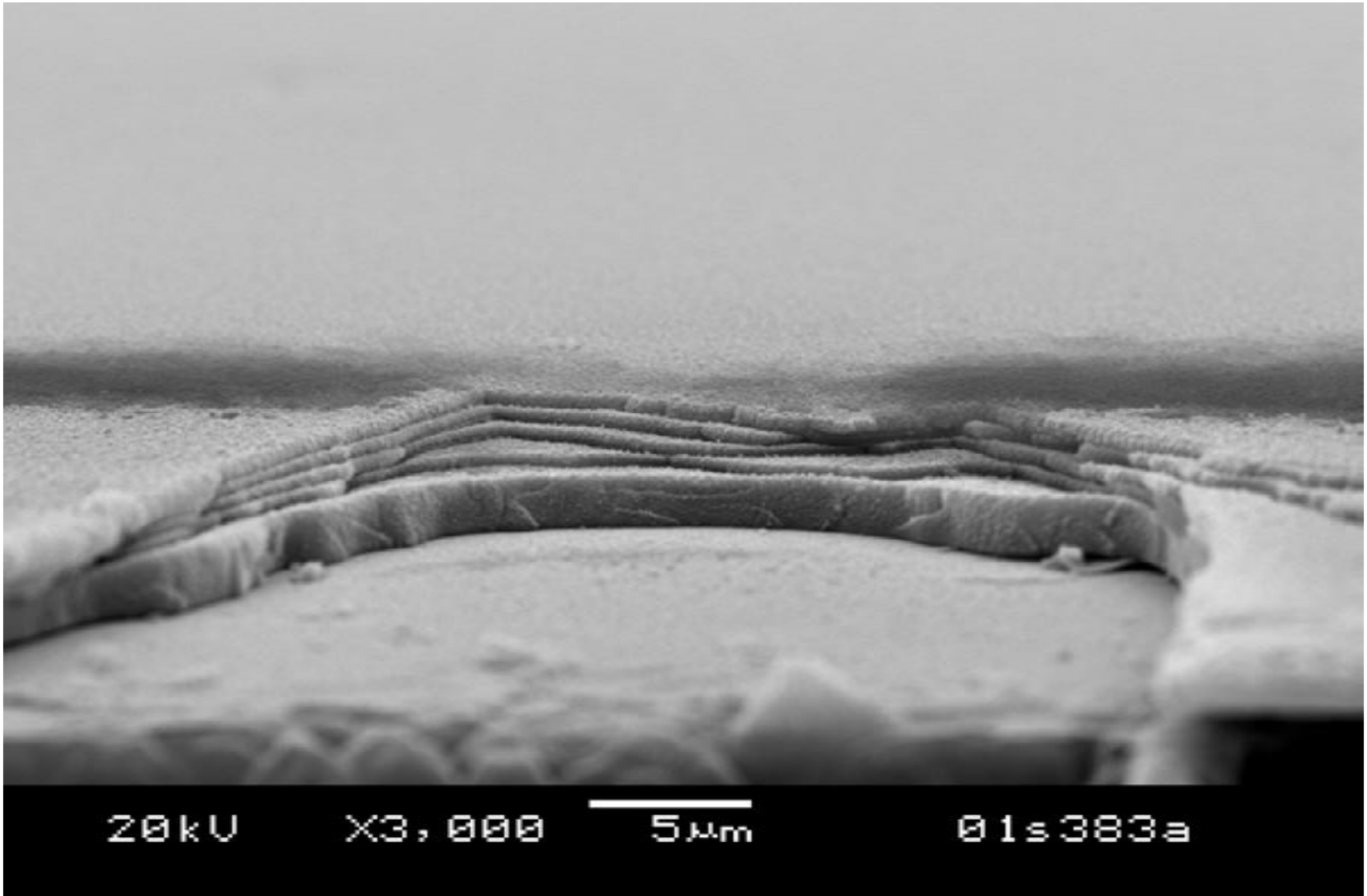
a) Basic 4 dyad structure

b) Barrier structure on OLED cathode

c) Barrier structure on substrate defect

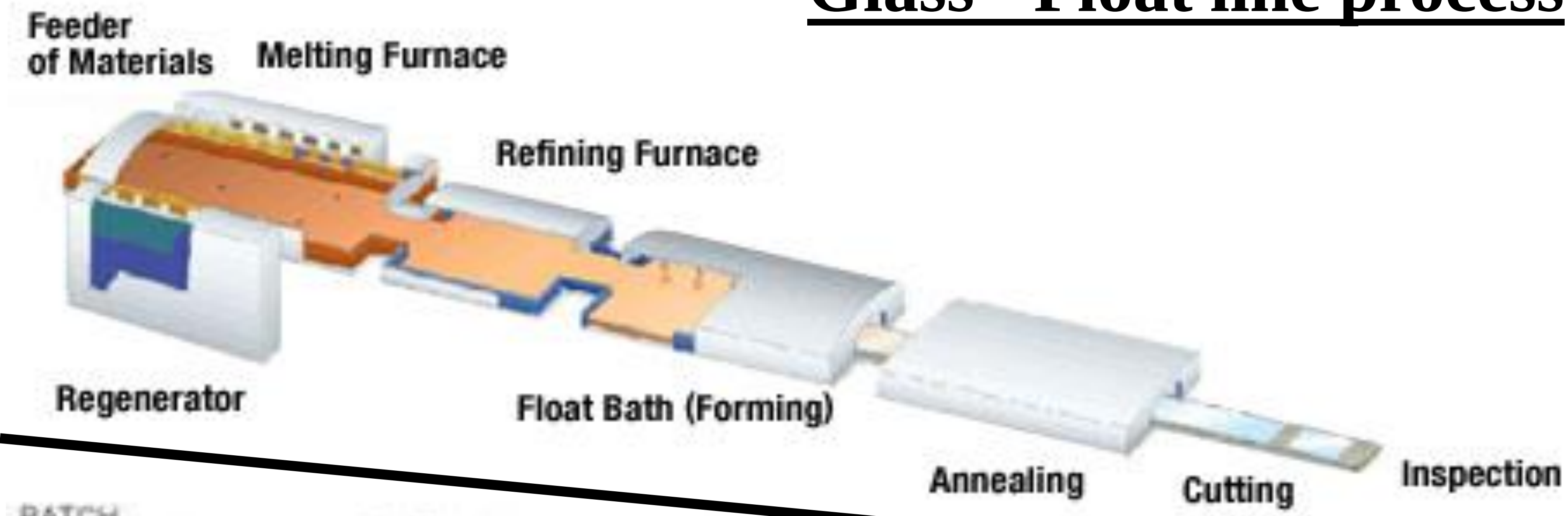
d) Basic polymer planarization layer on a test grating to evaluate planarising effect

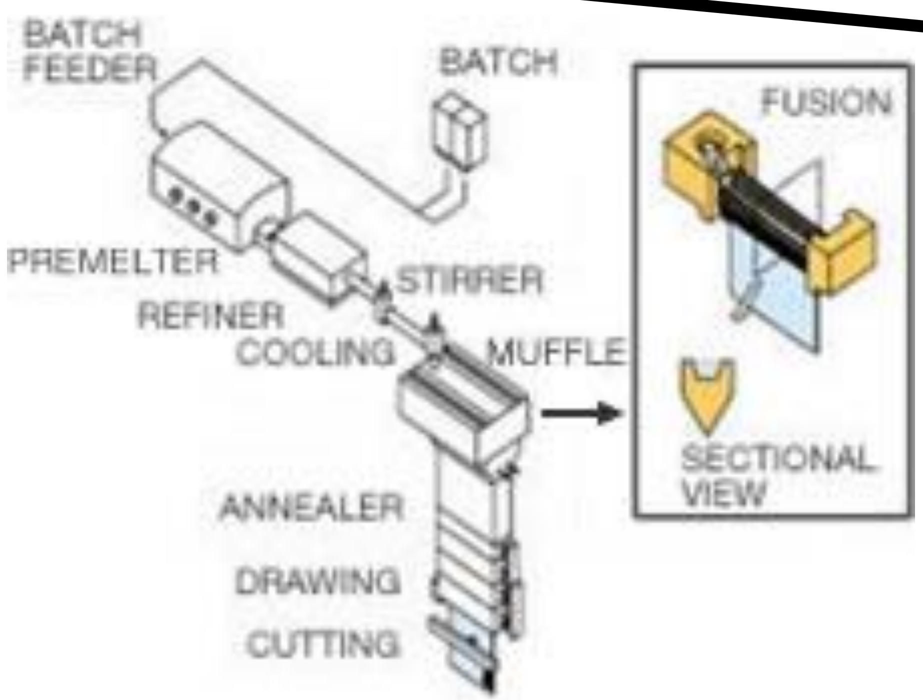
Multi-dyad barrier



Fracture cross-section SEM of generic Barix ™ film

Glass - Float line process



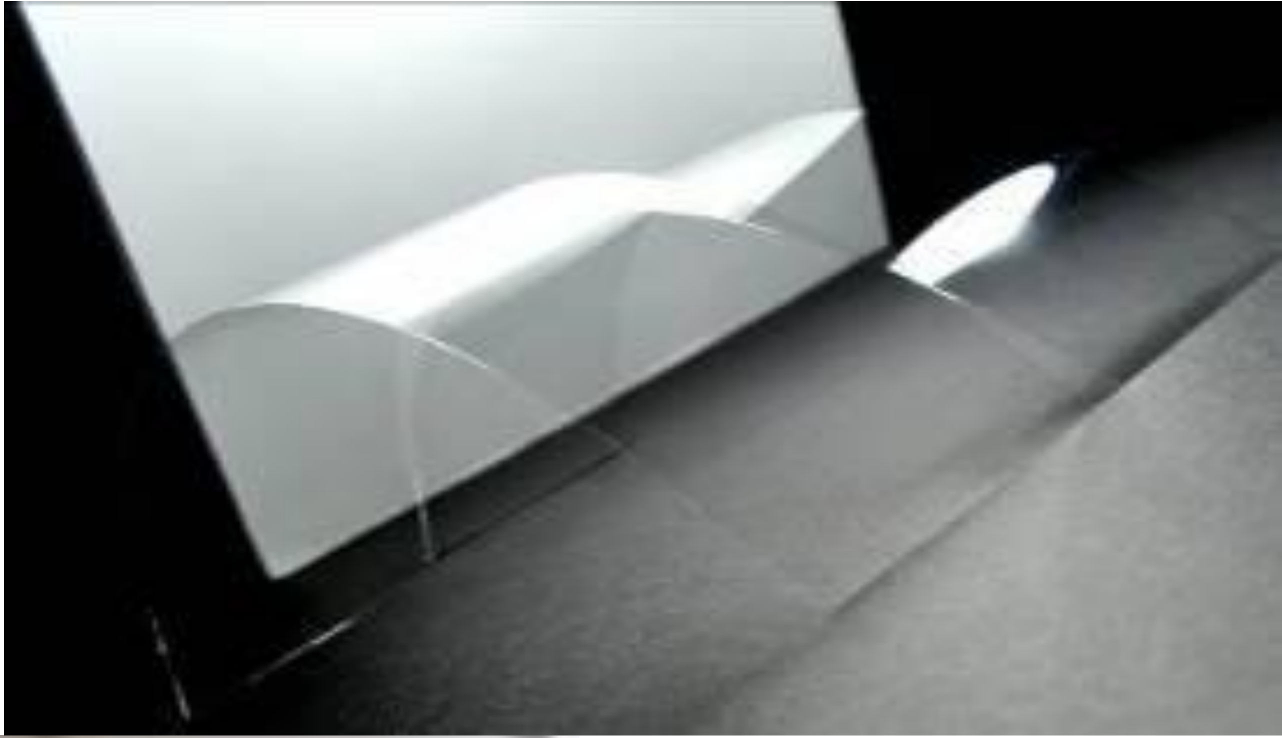


Fusion process

Rolls of glass down to 50 microns thick

Glass substrates

30 microns (R &D)
50 microns pilot production



The photograph from Corning shows the edges protected by Kapton tape

Conclusions

Key to good barrier:

Substrate quality

- **Surface – clean, smooth, flat, minimal defects**
- **Bulk - thermally stable, good gauge, well wound**
  zero or minimal exudate contamination

If you do not get the substrate right – do not bother coating

Deposition process

- **High quality winding – tension control**
- **Good quality deposition system hygiene**
- **Dense coating – minimise defects**
- **Maximise adhesion**
- **Minimal front surface contact – protect coating**
- **High quality handling & storing rolls**

Manage substrate surface (applies to: Dense coating – minimise defects; Maximise adhesion; Minimal front surface contact – protect coating)

Conclusions

All webs are contaminated with debris (both sides)

Most webs would benefit from a physical clean such as by tack-roll (both sides)

Many would also benefit from a molecular clean

to raise the surface energy

to modify chemistry to improve adhesion

Alternative strategy - cover debris using polymer coating - coating may also need plasma treating

Densify coating – minimise porosity & defects

CONSULTING LTD

Thank you for listening

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