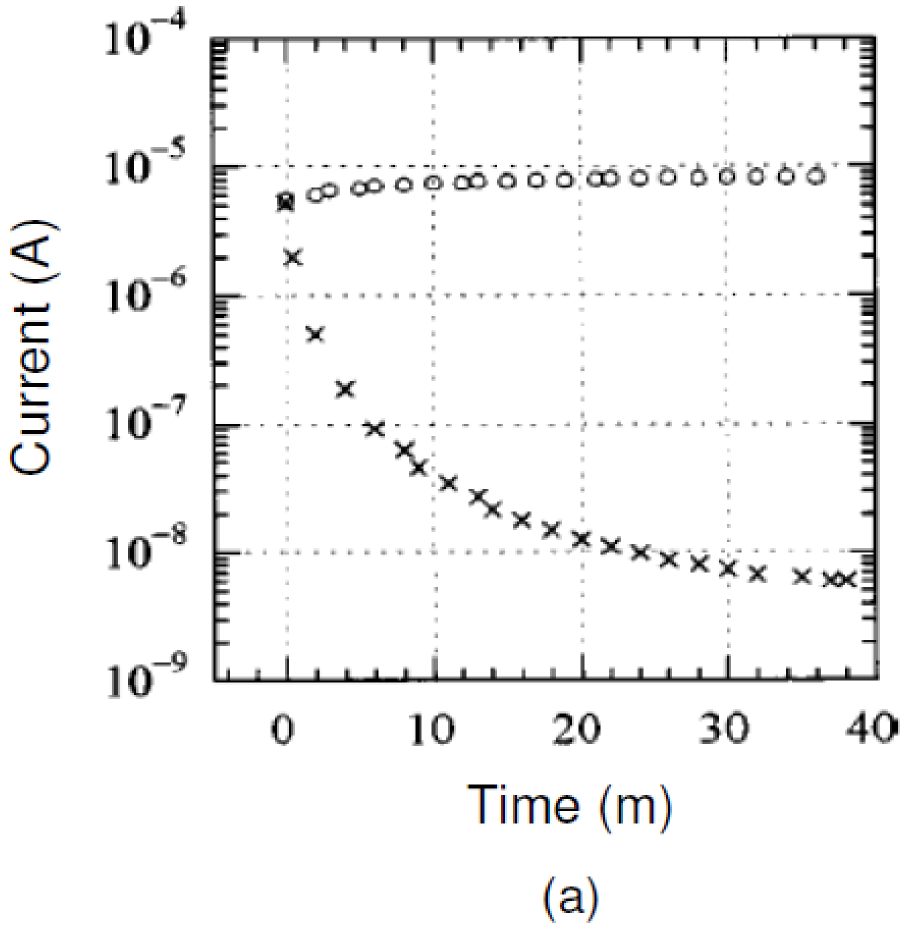
Organic Electronic Materials

Encapsulation & TCOs

Device performance degradation

- Gradation factors
  - Mechanical: Scratches, kinks, pressure,..
  - Reaction: moisture, oxygen, liquid chemicals (lipids from finger prints, acids, …)
  - Light induced: UV
- Encapsulation
  - Prevent water vapor, oxygen
- Water
  - Pixel shrinkage caused by water penetration from the side
  - Local degradation and dead-spot formation due to defects in the encapsulation



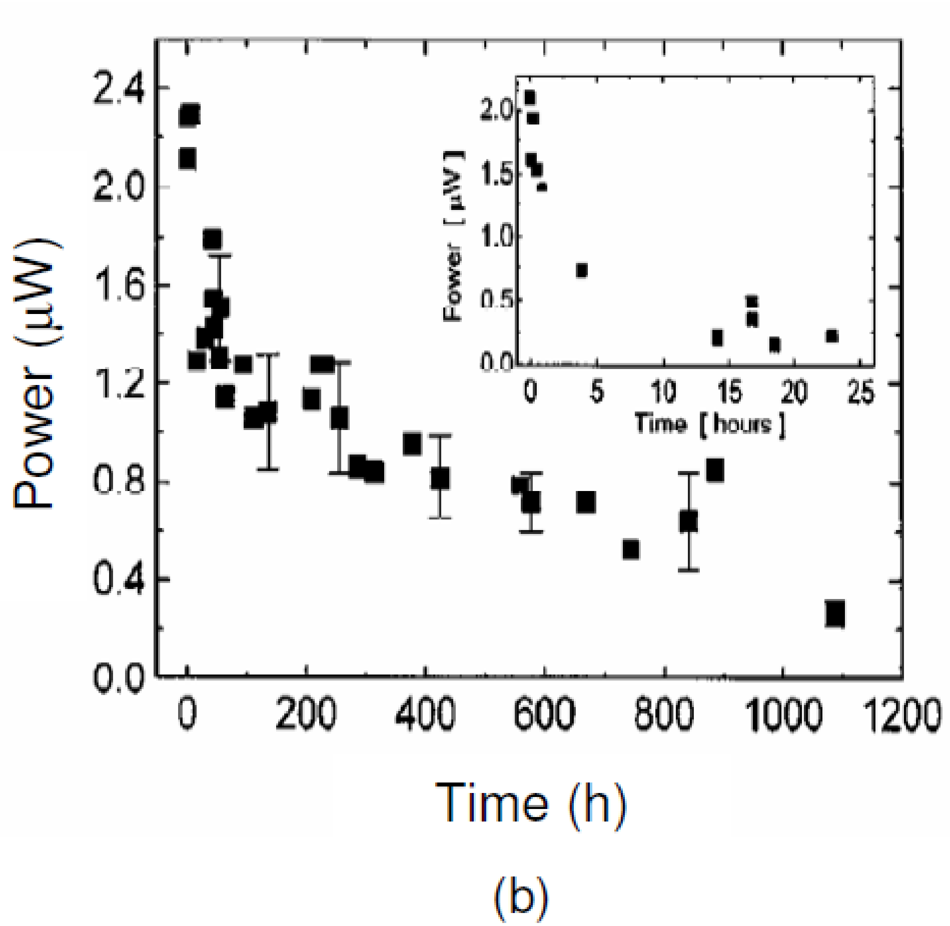
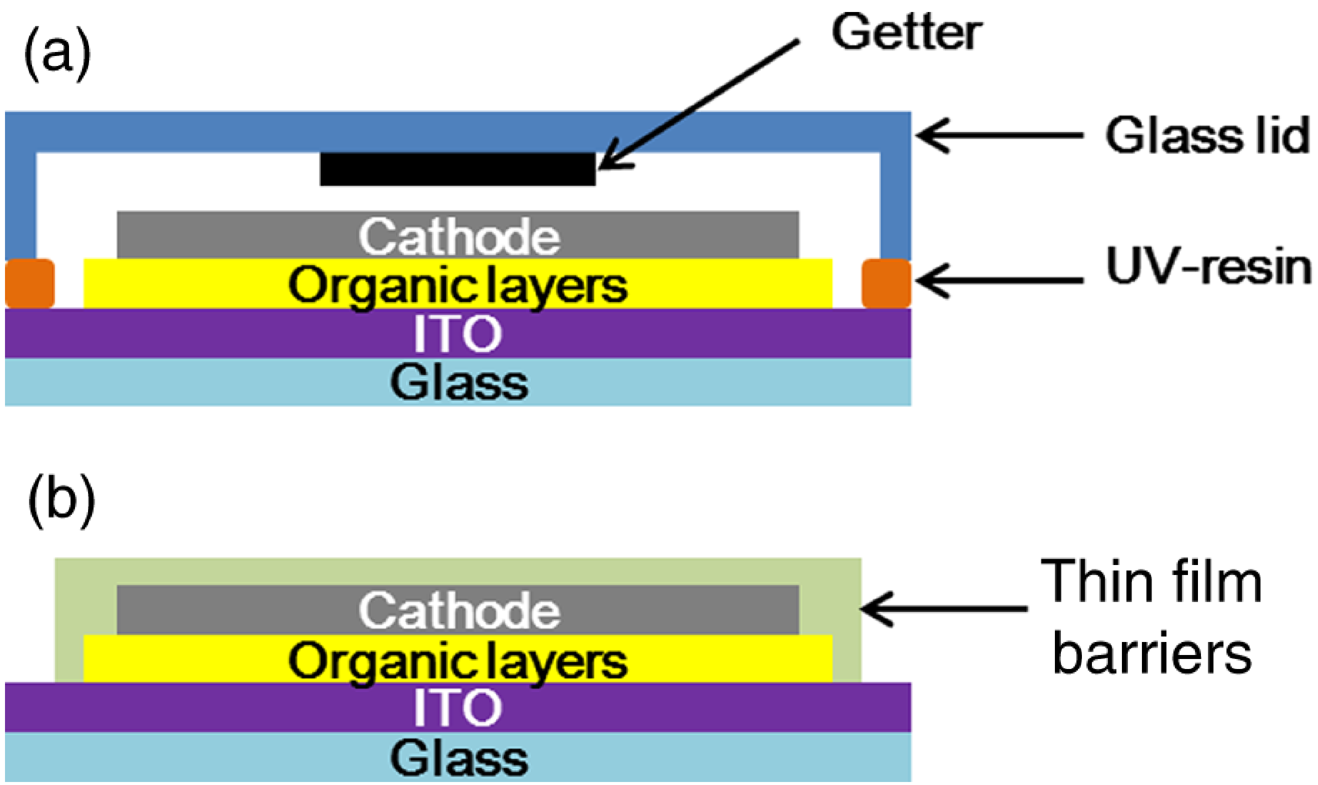
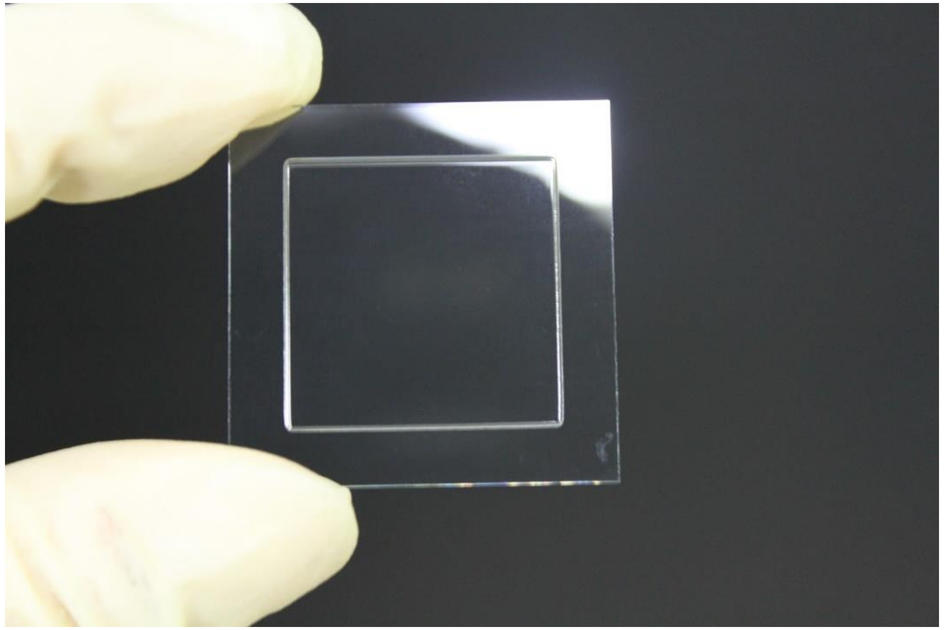
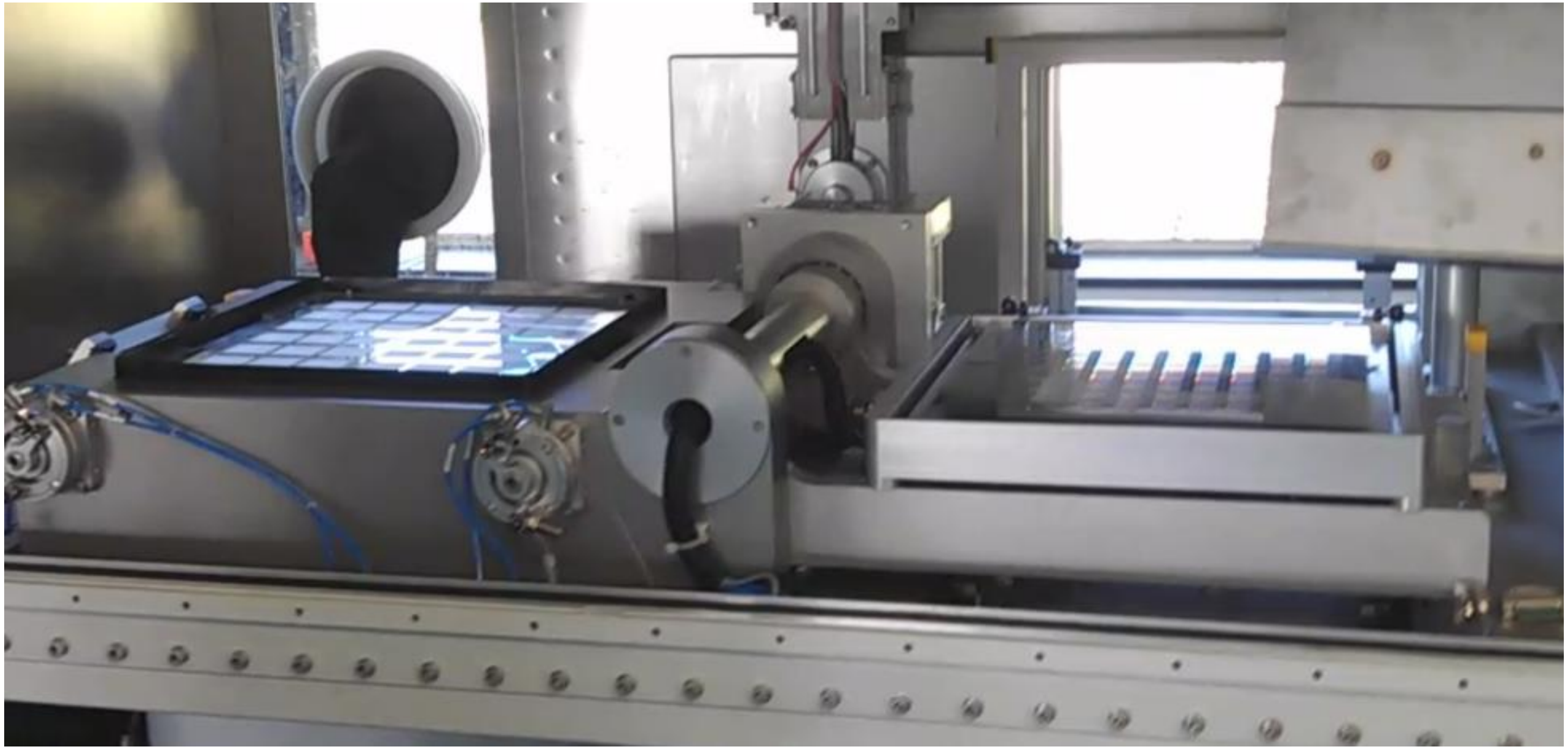


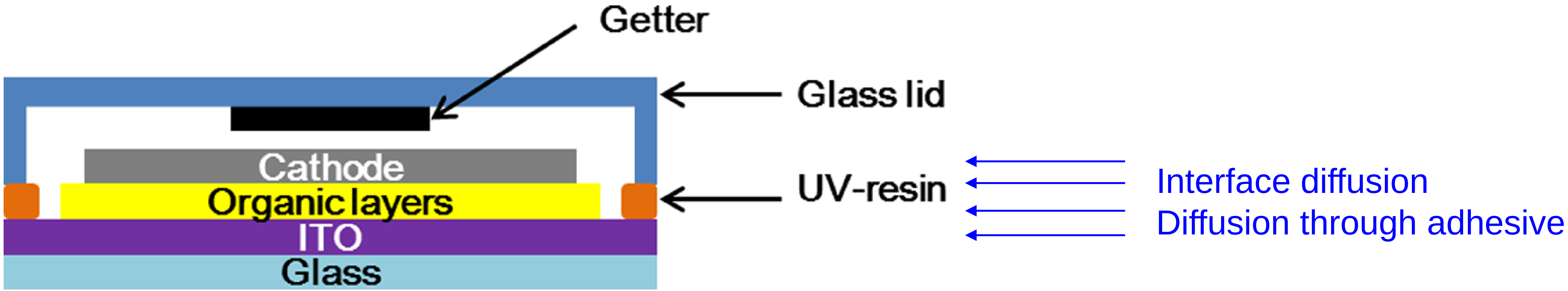
Figure 1.3 (a) Conductance decrease in ambient air for C_{60} thin-film FET at a source-drain voltage of 30 V without alumina covering (crosses) and with alumina covering (circles). Taken from reference. [18] (b) Optical power output of an encapsulated OLED device as a function of time. The inset shows the corresponding response of a bare OLED. Taken from reference.[19]

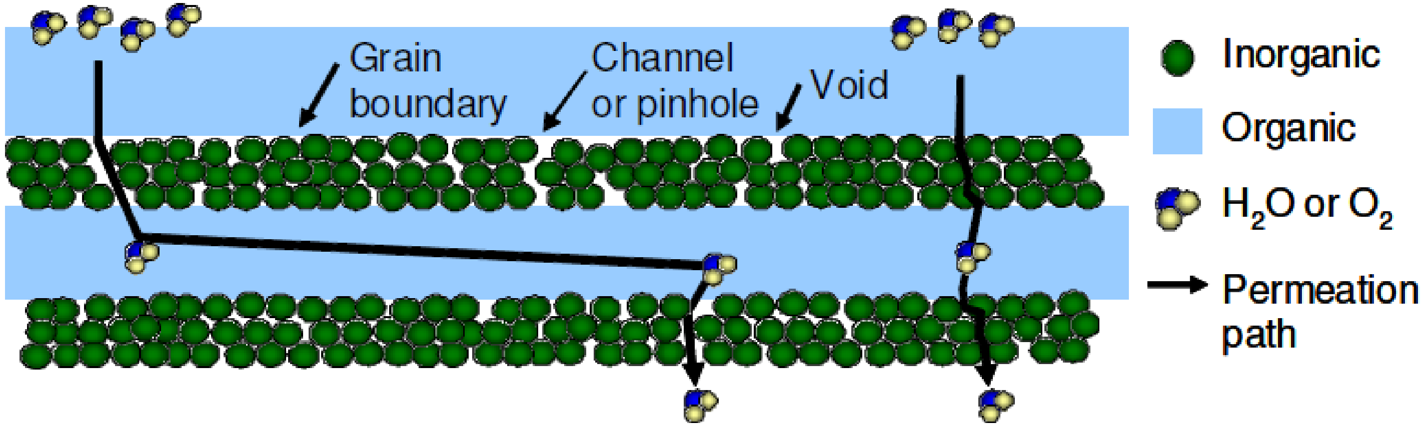

(a)
Getter
Glass lid
Cathode
Organic layers
UV-resin
ITO
Glass
(b)
Cathode
Organic layers
Thin film barriers
ITO
Glass



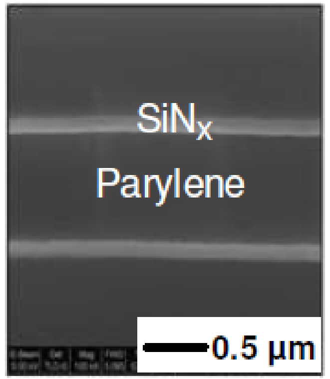


https://www.simac.com/en/simac-masic/equipment-engineering/solutions/lcd-led-oled-production-tool





(a)

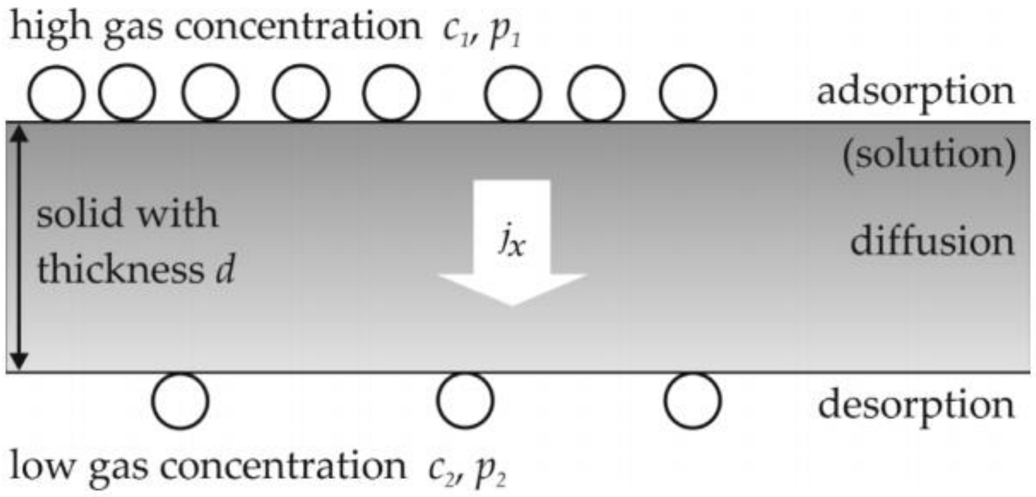


(b)

Tortuous water permeation path through organic/inorganic multilayer structure

Cross-section of organic/inorganic multilayer structure. Bright films are 100 nm-thick SiNx and dark film are 1 um-thick parylene.

Permeation in solid and thin films



$$P = D \cdot S$$

P: permeation coefficient

D: diffusion coefficient

S: sorption coefficient

1. Adsorption and solution

   The permeating gas is adsorbed at the surface of the solid, and if the gas is soluble in the material, it is dissolved in the solid.

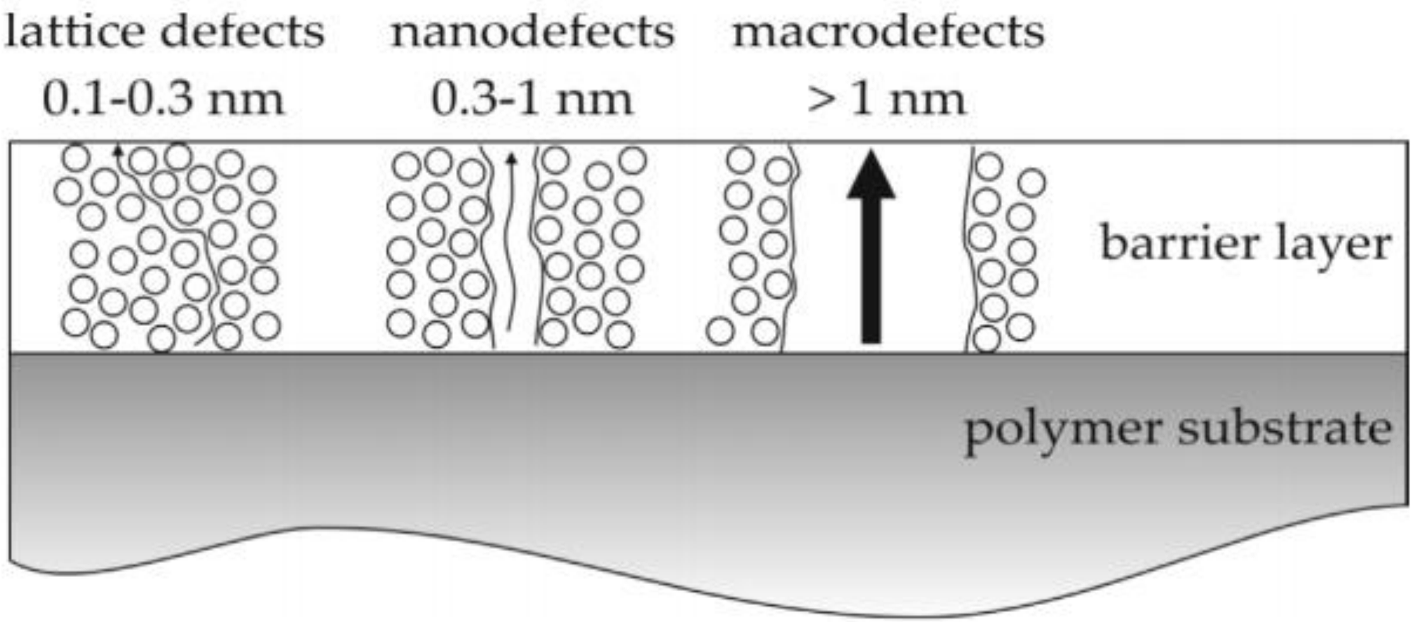
2. Diffusion

   Depending on the concentration gradient between the two solid surfaces, the gas diffuses through the solid material.

3. Desorption

   The gas particles are released from the backside solid surface.

- Permeation through a glass encapsulation: Fick’s permeation law
  - Thick glass → impermeable
- Permeation through a polymer web, organic layers, & adhesives: Fickian diffusion model
  - Assumption: the materials are free of local irregularities (defects) & homogeneous thickness & homogeneous material composition
- Permeation through metallic & oxide films: cannot described with Fickian model
  - Defects provide higher permeation



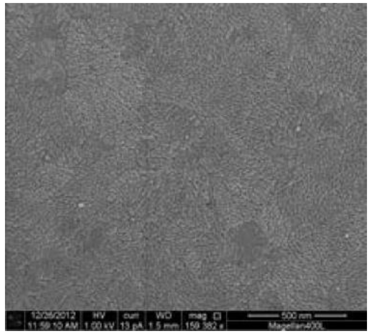
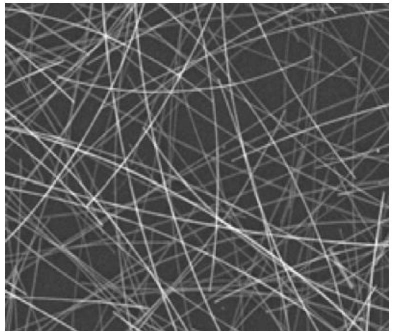
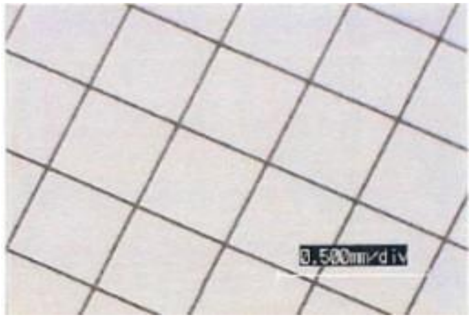
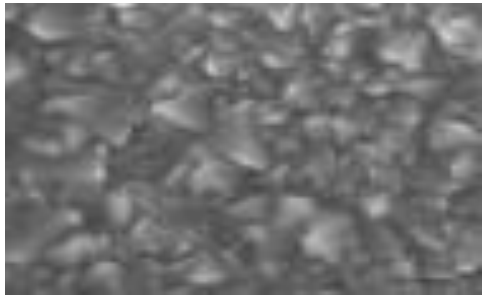
Polymer substrates for encapsulation

- PET, PEN
- Requirements
  - Uniform surface and low intrinsic surface roughness without spikes
  - Low density of particles and surface defects
  - High optical transparency and low absorption for front side encapsulation
  - Good adhesion of printed and/or vacuum-coated thin films on the polymer
  - Mechanical stability versus bending, strain, and also scratching
  - Temperature stability (~120°C ~ 150°C more or less)
- PI, PEEK: high temperature stability (~250°C ~ 300°C)
- ETFE (ethyletetrafluorethylene): UV & moisture stability

Transparent electrodes

Table 1. Main property requirements of a transparent electrode for some important applications. Plus signs indicate better values.

Application	Transparency	Conductivity	Flexibility
Photovoltaics	+++	+++	+
OLED/PLED	++	++	+
Film heaters	+	+++	++
Touch screens	+++	++	++

	ITO	NW	Metal Grid	FTO/AZO
				
Pros	• Well established	• Low cost solution process • Scalable • Flexible	• High conductivity (< 1 ~50 ohms/sq) • Flexible	• 10~20 ohms/sq • Compatible with glass production
Challenges	• Limited conductivity, especially on plastic • Brittle/not flexible • High cost • Expensive vacuum process	• 5 ohms/sq with >90% transmission	• Optically visible • Large openings → charge spreading • High thickness → needs dielectric/planarization • Lifetime issue: needs passivation	• Cost competitive only at very high volumes (inline with float glass process) • Brittle/not flexible • Roughness • High cost • Expensive vacuum process

* CapEx: capital expenditure (자본지출비율)

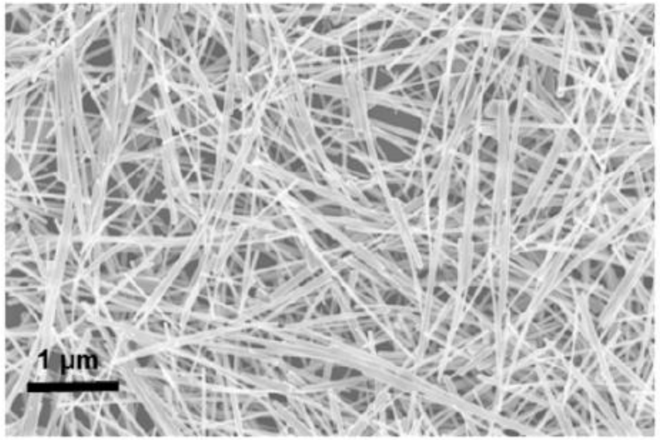
Table 2. General guide to transparent conductive material electrode fabrication.

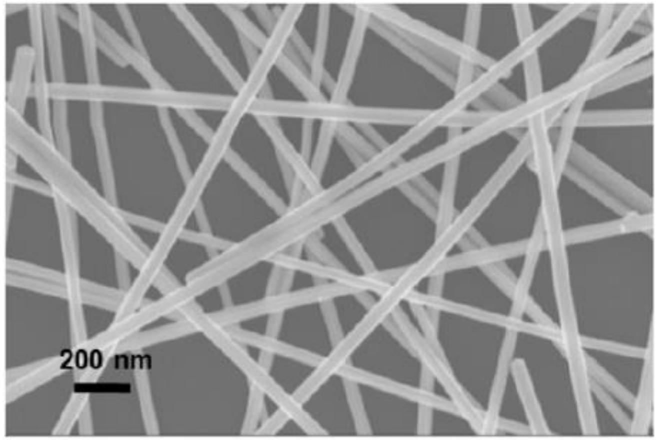
Fabrication method[a]	TCOs	Graphene	CNTs	AgNWs
Chemical vapour deposition	+++	+++	+	–
Sputtering	+++	–	–	–
Spin coating	–	+	++	++
Spray deposition	++	+	+++	+++
Screen printing	––	+	++	++
Cost	Low-high	High	High	Medium
Processing temperature (°C)	>200[b]–1000	RT–1000[c]	RT–700[c]	RT–700[c]
Uniformity	+++	+ to +++	++	++
Typical thickness (nm)	100–300	<5	<10	25 > 600[d]
Typical R_s ($\Omega/\square$)	5–100	30–5000	60–300	1–50
Typical transmission (at 550 nm)	80–97%	80–96%	80–91%	80–96%
Typical references	[9–13]	[14–19]	[11, 20–26]	[27–33]

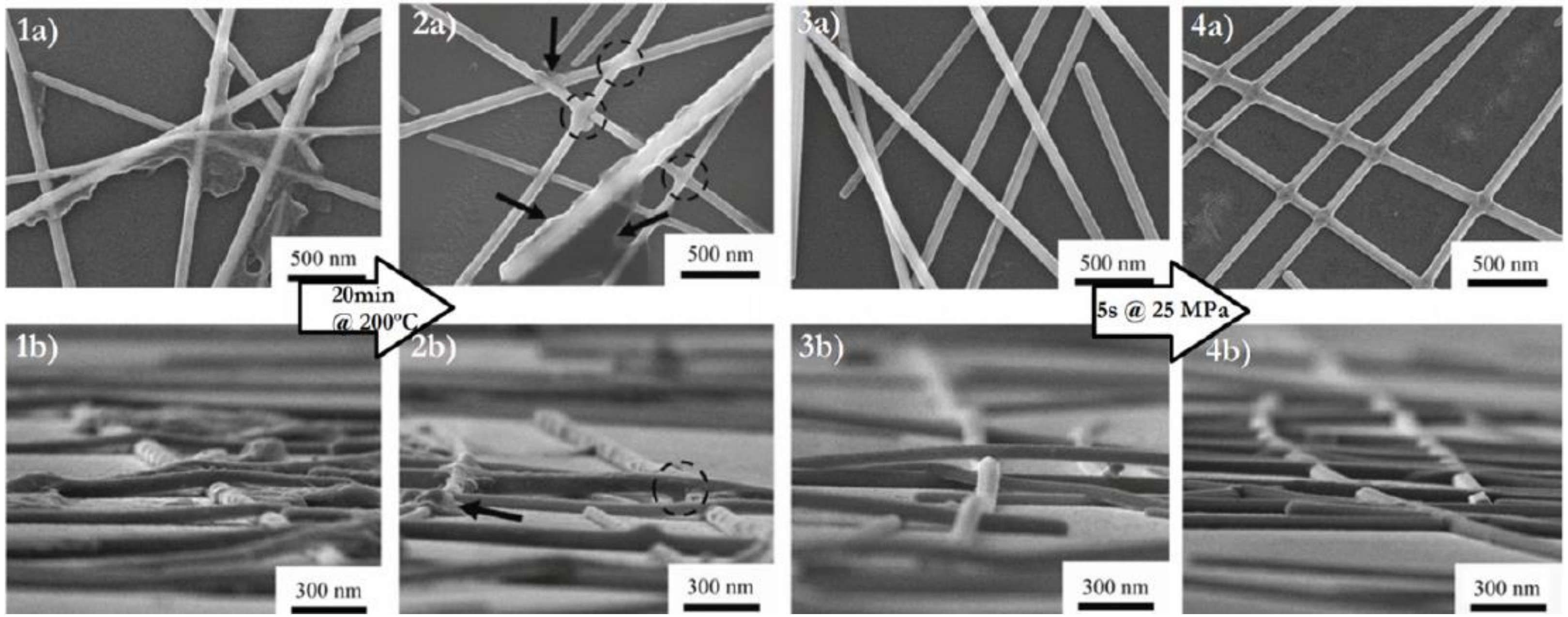
A. Fabrication method refers to the production of electrodes directly, not to the production of the constituent components which are used to fabricate the network.
B. Deposition temperatures of TCOs usually require several hundred degrees Celsius or the use of vacuum processes such as sputtering.
C. Networks can be fabricated at room temperature (RT) but if device fabrication requires high temperature processes vacuum or encapsulation are required to stabilize the films.
D. Thickness is diameter and density dependent though with high mechanical pressure it can be reduced to the diameter of a single nanowire

TCO (Transparent Conducting Oxide)
: ITO(Indium-tin oxide), FTO(SnO2:F), AZO(Al doped Zinc Oxide), ..

STM images of Ag NWs

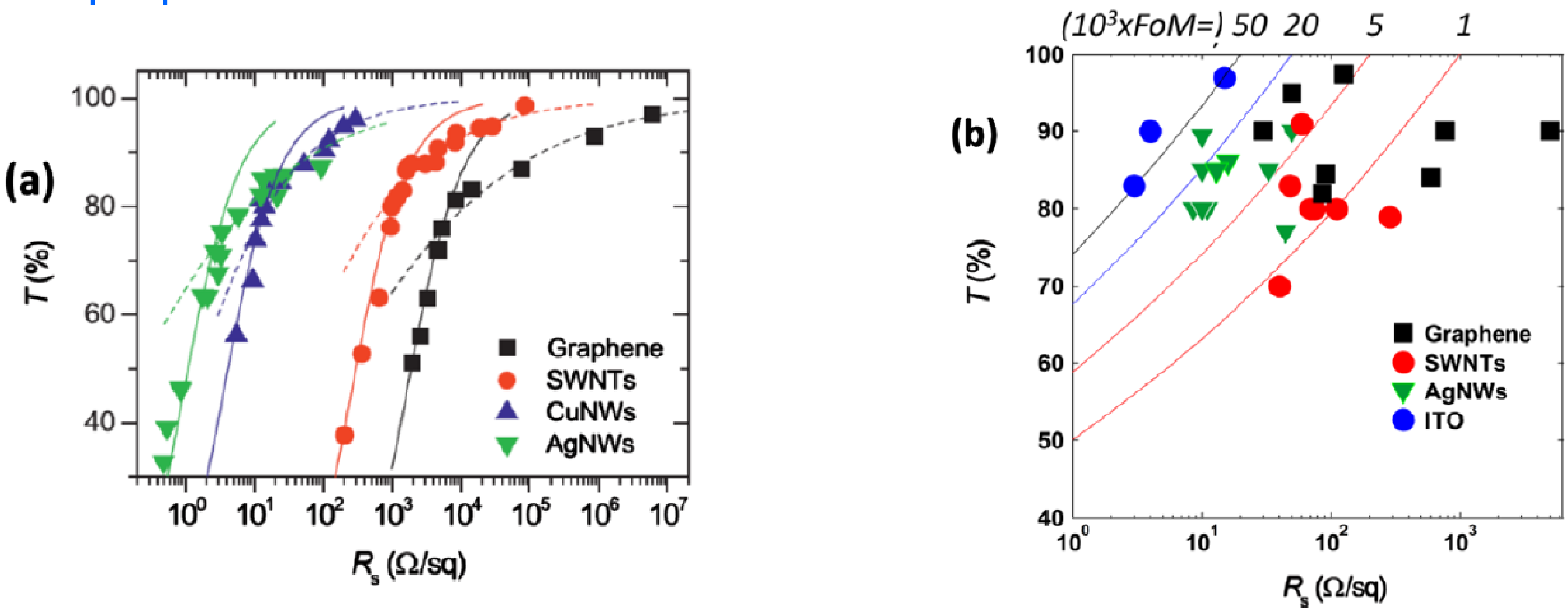






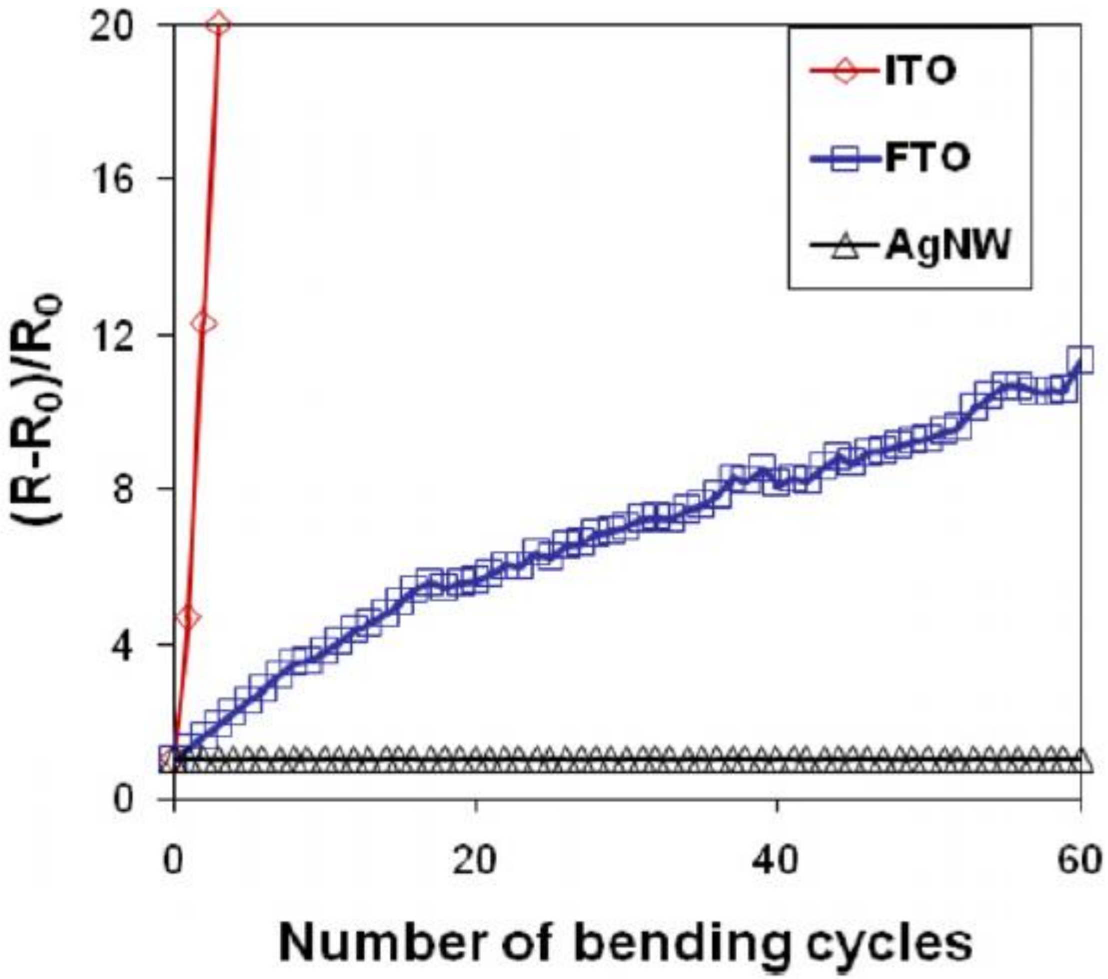
- SEM images of Ag NW networks
- (a) series : top-down view of the sample
- (b) series : off-angle cross-sectional vies.
- 1(a) & (b) : as-deposited NW networks.
- 2(a) & (b) : the effect of thermal annealing at 200 deg for 20 min.
- 3(a) & (b) : an as-deposited network after rinsing in water and ethanol
- 4(a) & (b) : the effect of 5s of mechanical pressure applied at 25 MPa.

Optical properties



(a) Optical transmittance (at 550 nm) versus sheet resistance for transparent conductors composed of nanostructured materials. Each set of points can be divided into two regimes: the bulk regime (solid line) and the percolation regime (dashed line).

(b) Optical transmittance (at 550 nm) versus sheet resistance for graphene, carbon nanotubes, AgNWs and ITO. Solid lines exhibit iso-values of the figure of merit



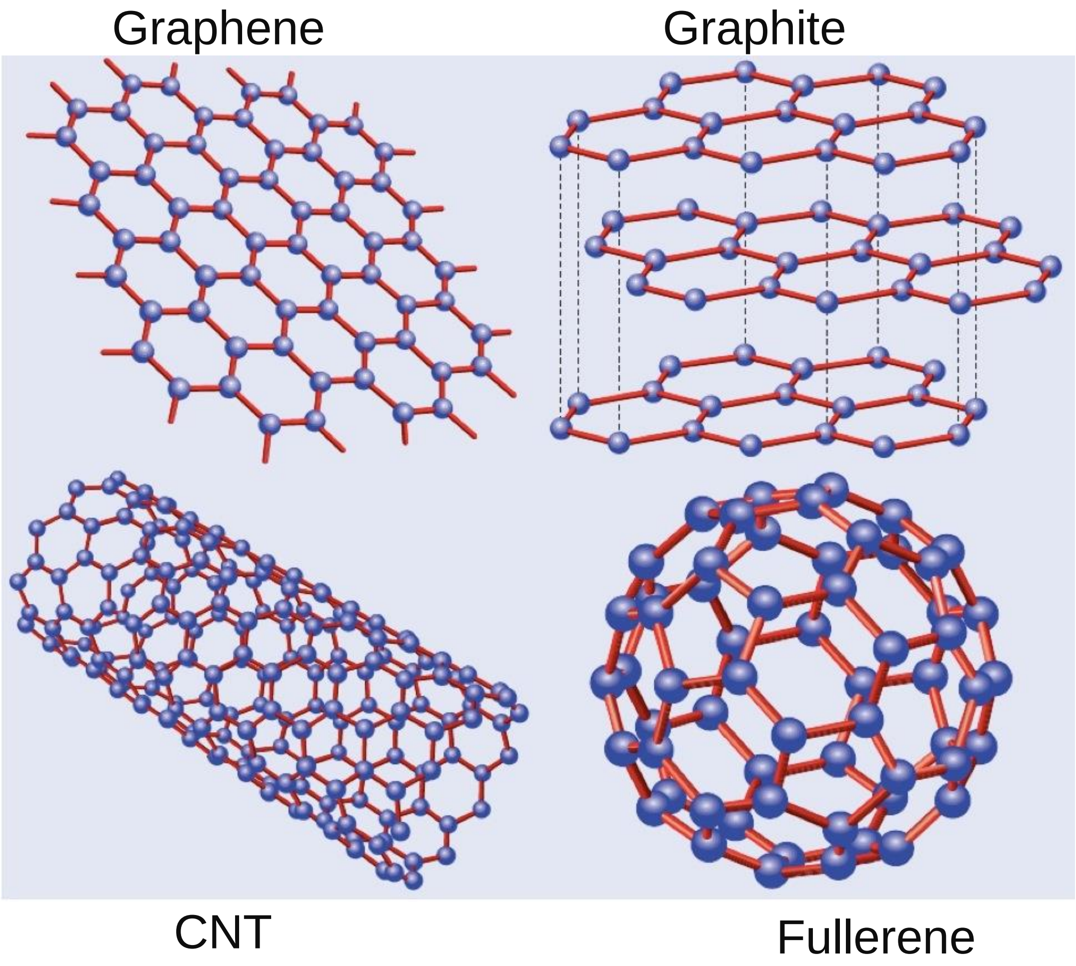
Comparison of TCMs under mechanical bending. During one cycle the specimen is flat, and then bent up to a radius of curvature of 5 mm, and returned to the initial position. The TCM is on the opposite side to the bending radius and is therefore placed under tension

https://pdfs.semanticscholar.org/da72/ca83139763843679fd994d8b840d2b8f2d6b.pdf

Graphene

- 2-dimensional, crystalline allotrope of carbon
  - Allotrope: property of chemical elements to exist in two or more forms
- Single layer of graphite
  - Honeycomb (hexagonal) lattice

- Studies on graphite layer Studies on graphite layers for past hundred years
- Graphene theory first explored by P.R. Wallce (1947)
- Andre Geim & Kontantin Novoselov Nobel Prize (2010)
- Physics observed using TEM



Electronic structure of graphene

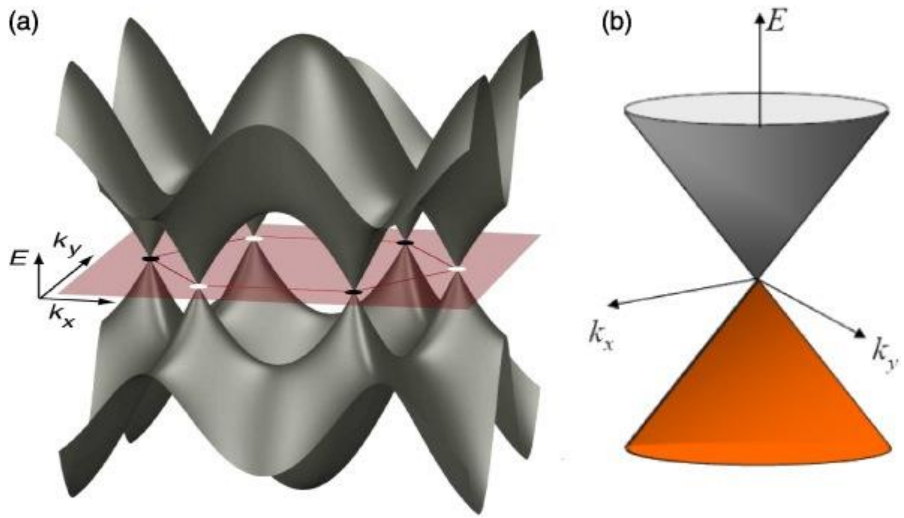


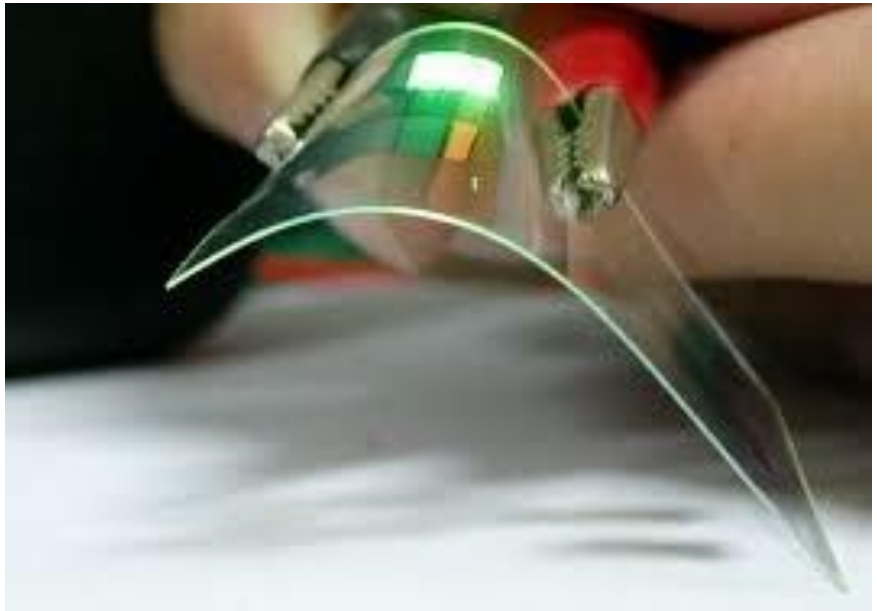
Table I Values of electron mobility and energy bandgap for Hall effect sensor materials

	μ(cm^2 V^{-1} s^{-1})	E_g (eV)
Silicon	1,900	1.12
GaAs	8,800	1.43
InSb	78,000	0.17
InAs	33,000	0.35
InP	4,800-6,800	1.29
2-DEG	6,500-13,000	0.6-1.8

- Dirac Points are the transition between the valence band and the conduction band
- Part (b) shows that the dispersion relation close to the K points looks like the energy spectrum of massless Dirac particles
- Graphene electrons are like photons in mobility due to lack of effective electron and hole mass
- Experimental graphene's electron mobility is 15,000 cm^2/(V*s) and theoretically potential limits of 200,000 cm^2/(V*s)
- These charge carriers are able to travel sub-micrometer distances without scattering
- Fermi level: can be changed by doping

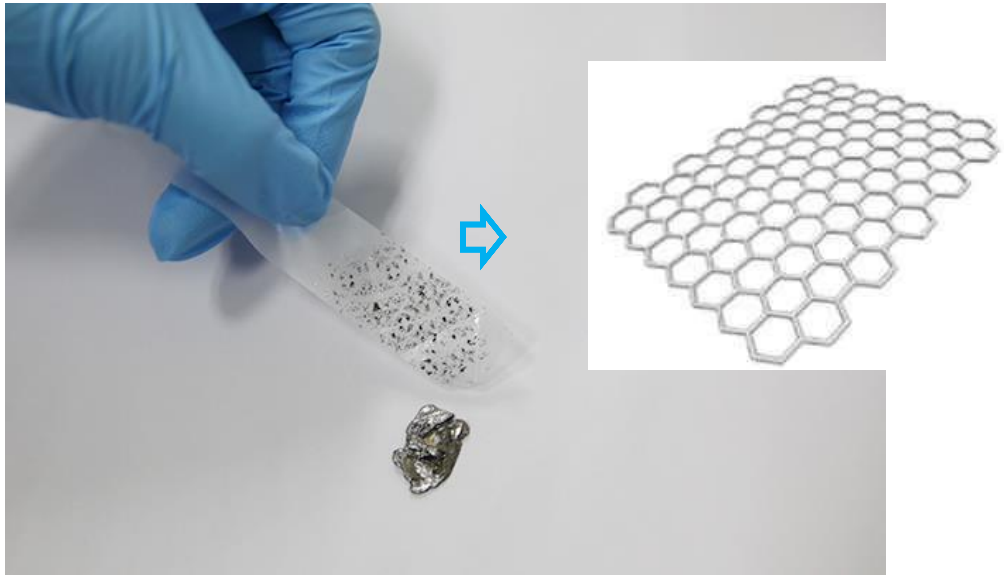
Optical properties of graphene

- Absorbs 2.3% white light
- Optical electronics absorb <10% white light
- Highly conductive
- Strong and flexible



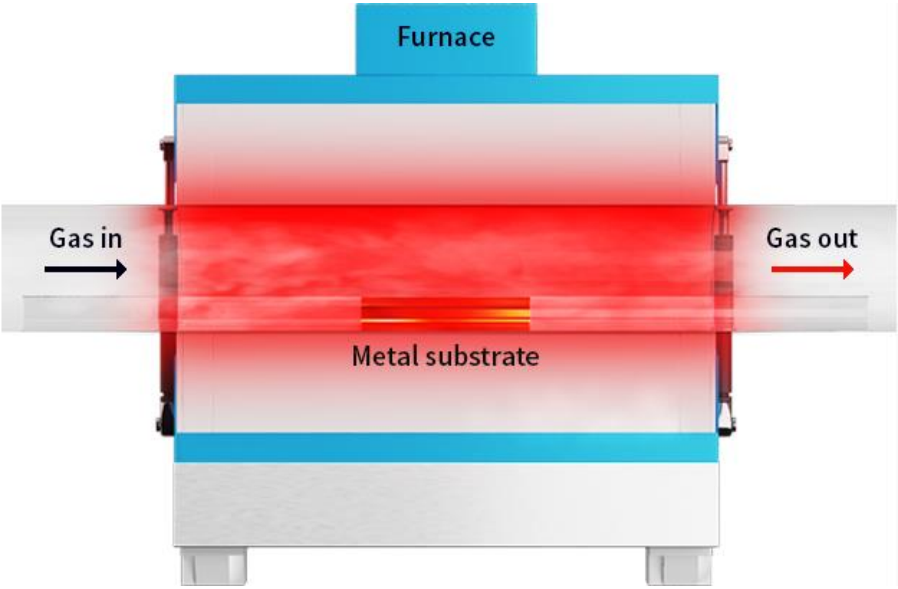
기계적 박리법

- 다층으로 구성된 흑연 결정에서 기계적인 힘으로 한 층을 벗겨내어 그래핀을 만드는 방법
- 2004년 노보셀로프와 가임 교수가 처음 발명한 방법
- 테이프의 접착력을 이용해서 떼어냄
- 크기와 형태를 제어할 수가 없어 소자 및 전극재료 등 다양한 형태로 응용이 제한



화학기상증착법 (CVD)

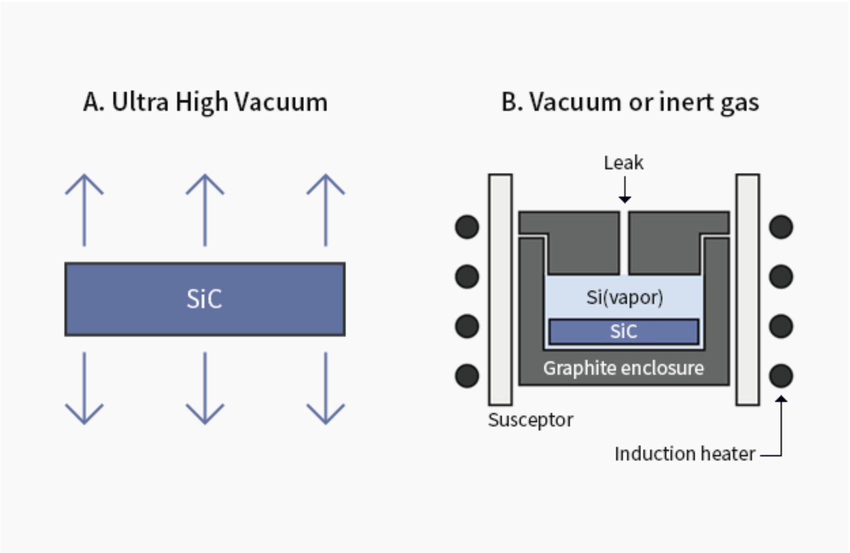
- 고품질 대량생산에 가장 많이 이용
- 메탄과 같은 탄소원을 이용해 기판에 직접 성장
- 고온에서 탄소 또는 합금을 잘 형성하거나 탄소와의 흡착성이 우수한 전이금속을 촉매로 사용하여 그래핀을 합성하는 방법 (Cu)
- 원하는 용도에 맞게 응용이 가능



http://www.graphenesq.co.kr/whatis/how.asp

Epitaxial 합성법

- SiC와 같이 탄소가 결정에 흡착되거나 포함되어 있는 재료를 약 1500도의 고온에서 열처리하여 생성
- 열처리 공정 중 탄소가 SiC 표면의 결을 따라 성장하면서 그래핀 형성
- 웨이퍼 크기까지의 균일한 그래핀 필름을 만른 수 있으나, 상대적으로 전기적인 특성이 좋지 않으며 기판의 비용이 높이 소자 제작에 어려움



화학적박리법

- 강산을 이용하여 흑연을 산화시켜 그래핀 층을 분리하는 방법
- 용액에 북산된 산화 흑연(graphite oxide)은 강한 신수청으로 인해 물 분자가 면과 면 사이로 삽입되어 멀어짐. 이를 초음파 처리하면 그래핀을 박리할 수 있음. 이렇게 만든 산화그래핀(graphene oxide)은 환원과정을 거쳐 그래핀으로 되돌림.
- 그래핀 대면적 성장과 대량생산을 만족할 수 있는 방법으로 흑연의 산화-환원 특성을 활용
- 산화성 그래핀 시트 생산이 용이하나, 환원공정에서 불순물이 발생하는 단점이 있음