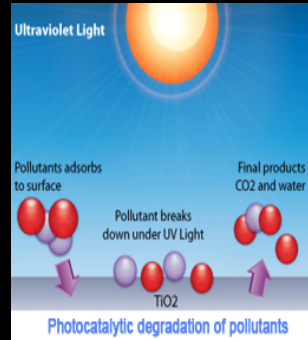


Advanced application of Thin Films part 2

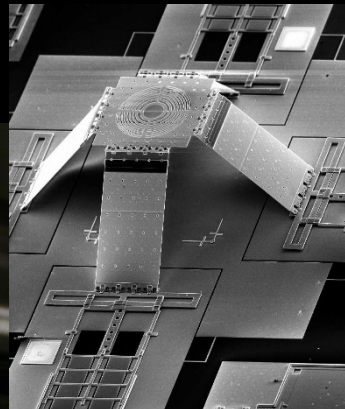
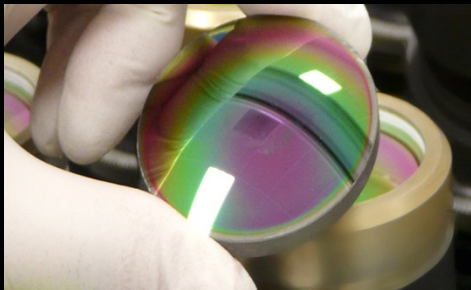
Jari Koskinen

Function and utility



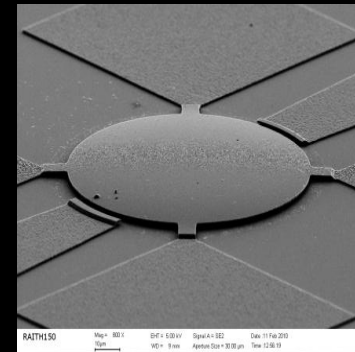
Titanium Dioxide: Photocatalytic activity

Optical systems, optical MEMS



Indium Tin Oxide, ITO:
Defrosting coating

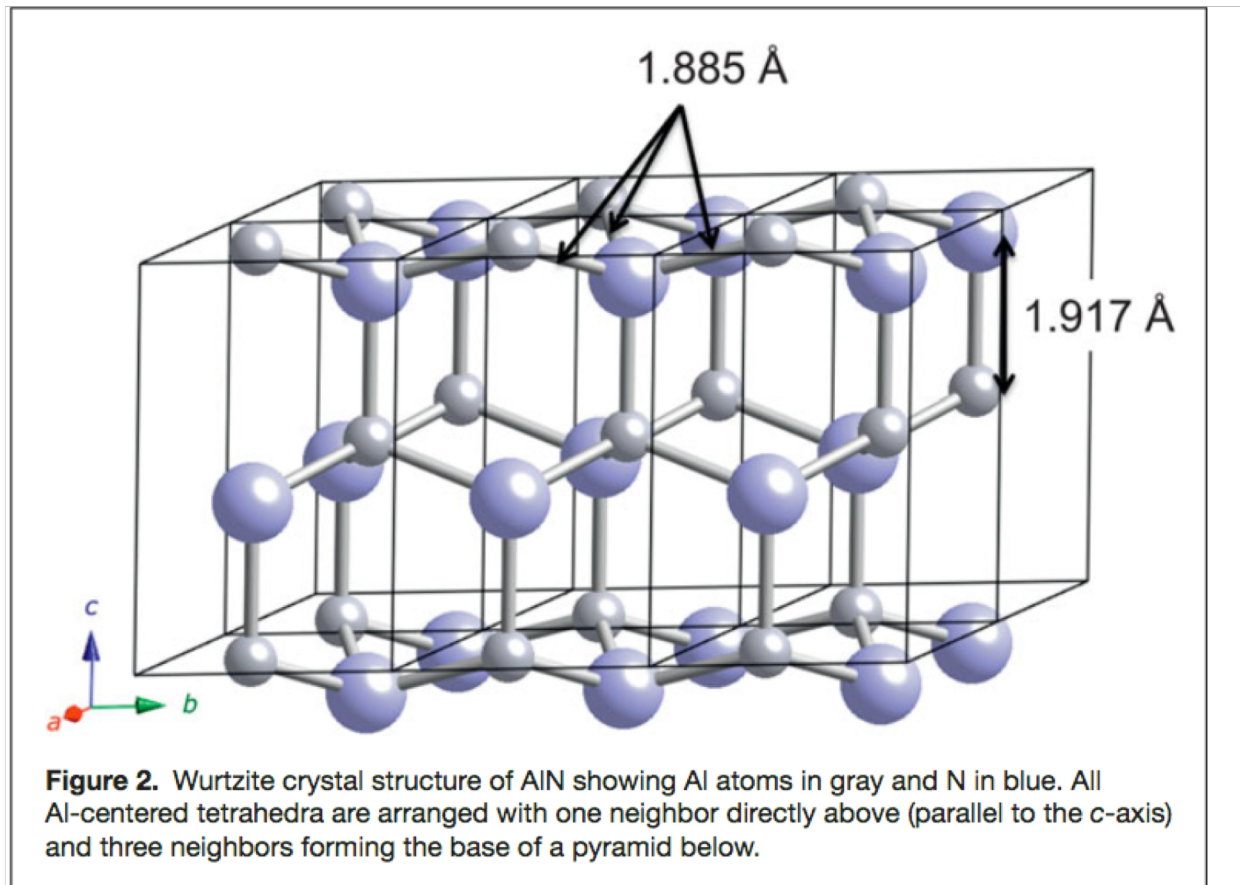
Microelectromechanical systems, MEMS

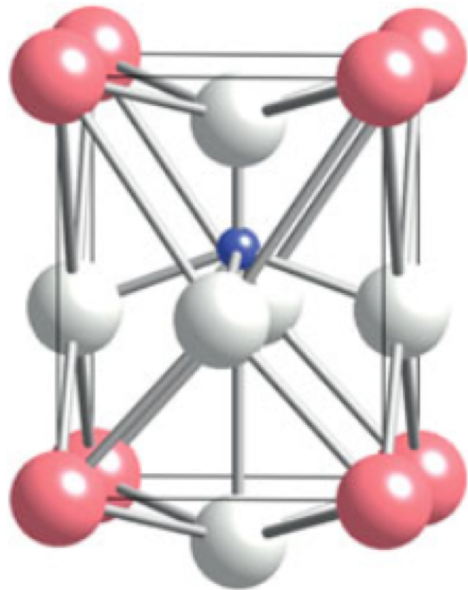


Part 2

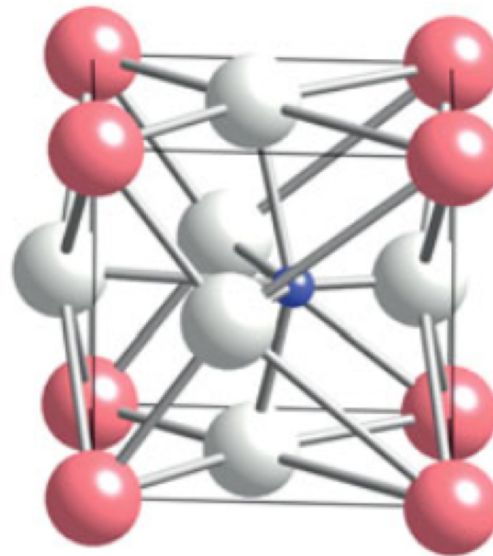
- **Energy harvesting (piezo)**
- **Optical coatings**
 - Tunable transmission
- **Magnetic Films for Data Storage**
 - Magnetic discs
- **Sensors**
 - Gas sensors
 - Electro chemical sensors
- **Photocatalytic TiO₂**

Piezo thin films

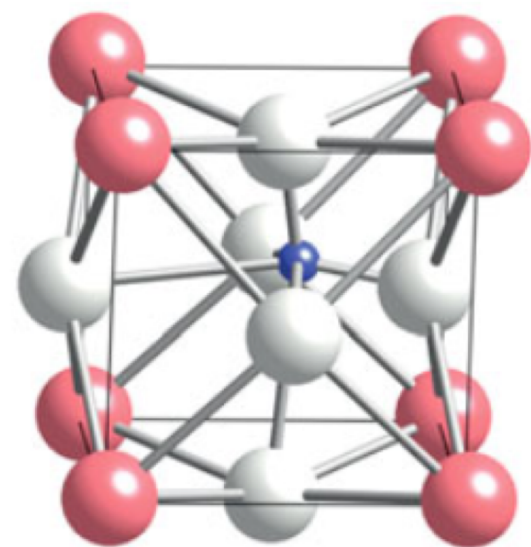




Tetragonal



Orthorhombic



Rhombohedral

Figure 3. Typical ferroelectric distortions (exaggerated for clarity) of the perovskite ABO_3 structure; the A ions (red) are at the corners of the unit cell, the B ions (blue) are close to the center of the unit cell, and the O ions (white) are near the face centers. Upon developing spontaneous polarization, a spontaneous strain also develops.

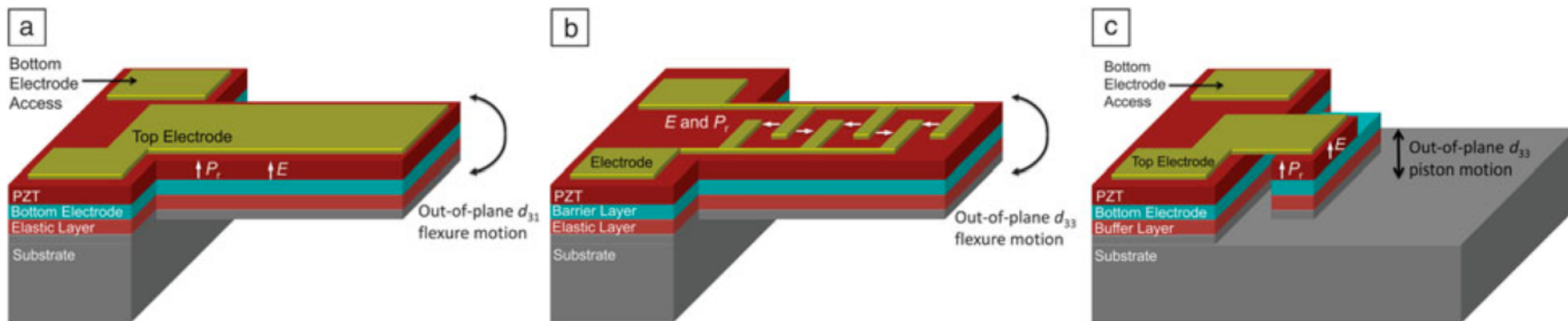


Figure 5. Illustration of common sensing and actuation modes in piezoelectric microelectromechanical systems. (a) Bending mode induced by $e_{31,f}$ (sometimes called d_{31} mode) for a film with top and bottom electrodes. The unimorph structure bends when lateral contraction of the piezoelectric layer acts on the passive elastic layer. (b) Out-of-plane bending due to in-plane expansion of d_{33} actuated-structure using interdigitated electrodes. In order to confine the electric field in the plane of the device, the layers underneath the piezoelectric should be electrically insulating. Barrier layers such as ZrO_2 or HfO_2 are typically required to prevent reaction between lead-based perovskites and Si or SiO_2 elastic layers. (c) Piston motion due to the out-of-plane d_{33} coefficient. Note: PZT, $Pb(Zr,Ti)O_3$; E , electric field; P_r , remanent polarization.

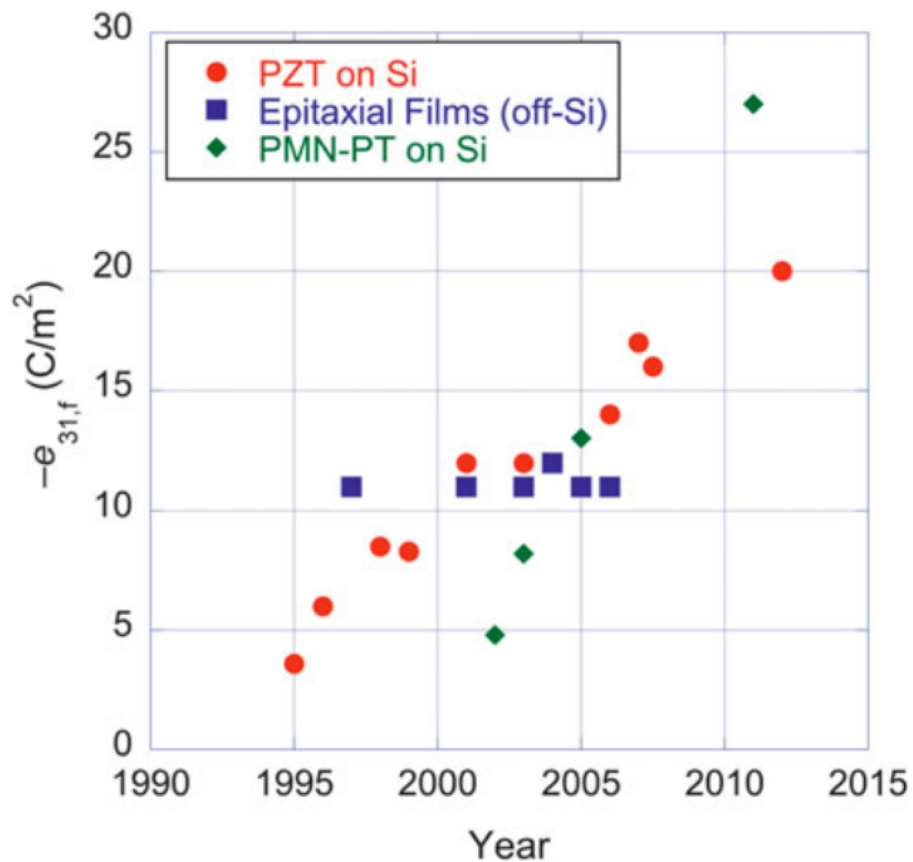
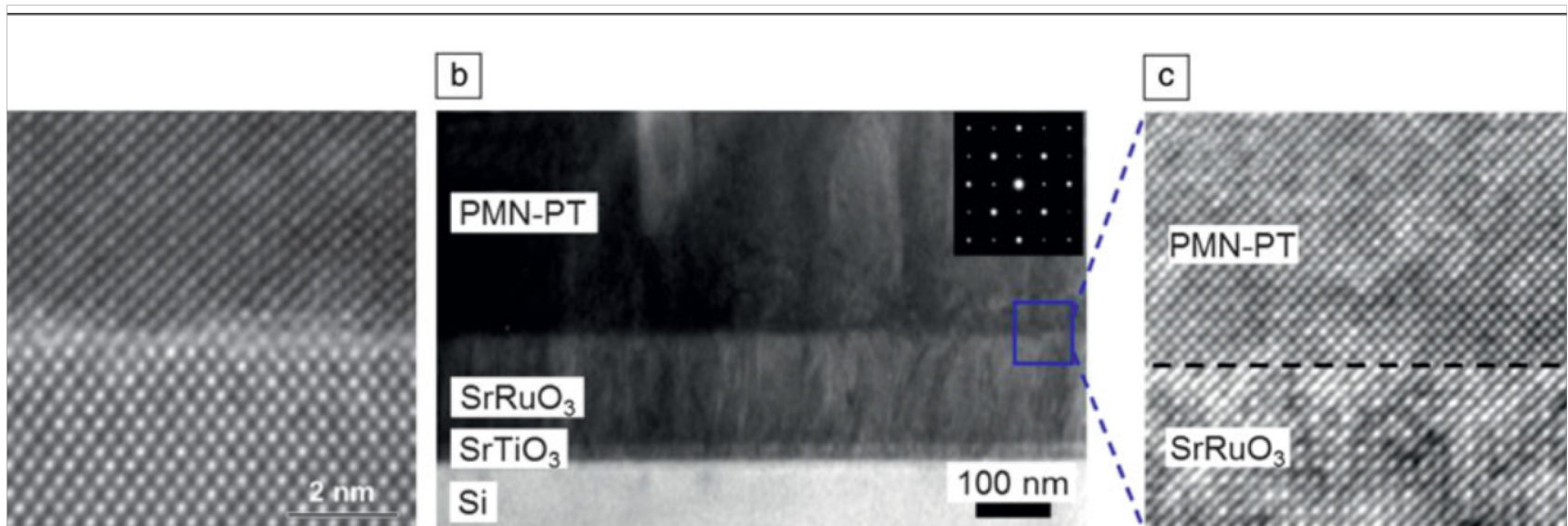
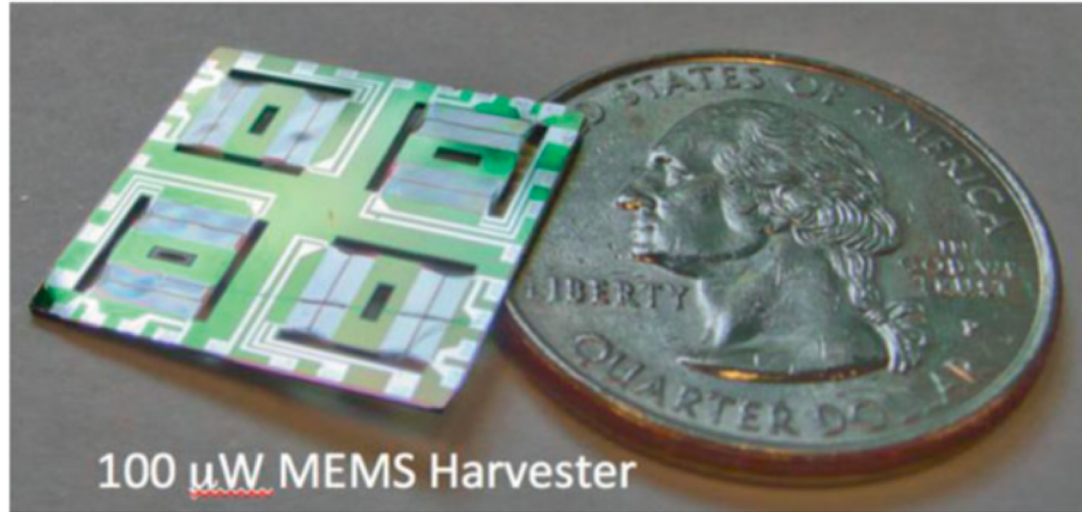


Figure 6. Evolution in piezoelectric $e_{31,f}$ coefficients, showing comparisons to data for bulk PZT materials. Data courtesy of P. Muralt. Adapted from Reference 45. Note: PZT, $\text{Pb}(\text{Zr,Ti})\text{O}_3$; PMN-PT, $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$.



(a) High resolution transmission electron microscope (TEM) image of epitaxial SrTiO_3 on silicon grown by molecular beam epitaxy (courtesy of Xiaoqing Pan of the University of Michigan and Darrell Schlom at Cornell University.) SrRuO_3 can then be epitaxially grown on top of the SrTiO_3 by off-axis sputtering to serve as the templating layer for the piezoelectrics, as well as a bottom electrode. (b) Low-magnification cross-sectional TEM image of an epitaxial $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ (PMN-PT)/ SrRuO_3 / SrTiO_3 thin-film heterostructure. The inset shows the selective area electron diffraction pattern of the PMN-PT layer along the $[100]$ zone axis showing a $\sqrt{3}\times\sqrt{3}$ superlattice. (c) High-resolution TEM image of PMN-PT and SrRuO_3 interface. (b) and (c) are adapted from Reference 65.

a



b

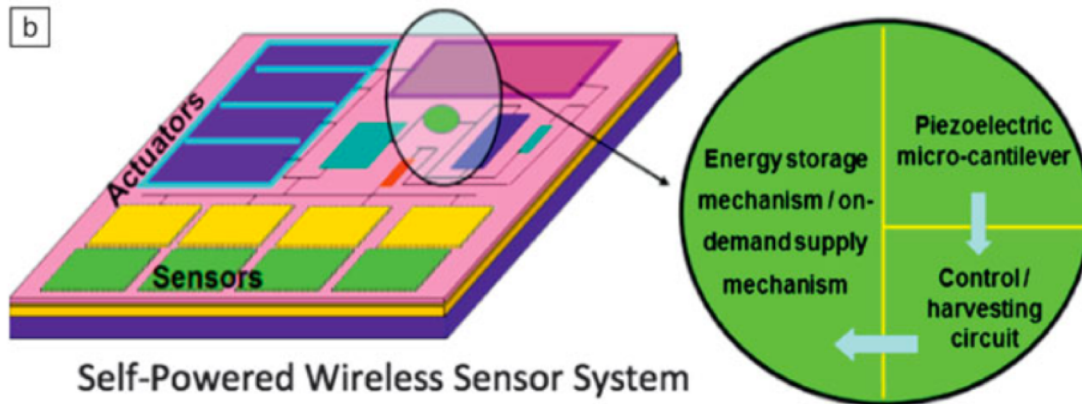
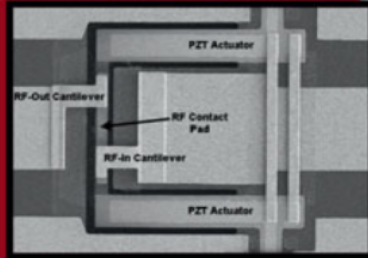


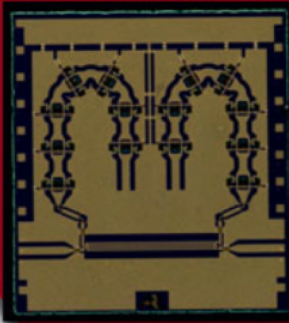
Figure 9. Examples of piezoelectric energy harvesting systems. (a) Photograph of a compact piezoelectric microelectromechanical system (MEMS) energy harvesting device, which is about the size of a US quarter (\$0.25) coin. A doubly clamped beam acts as a frequency locked loop, resulting in wide bandwidth, non-linear resonance. (b) Schematic of on-chip architecture for a self-powered wireless sensor network system. Robust self-powering can be achieved by utilizing all environmental energy resources, as well as dual purpose sensors and actuators, which also act as energy harvesters.⁸⁷

RF MEMS

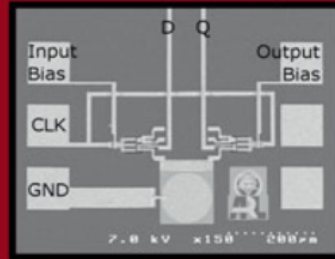
Switches



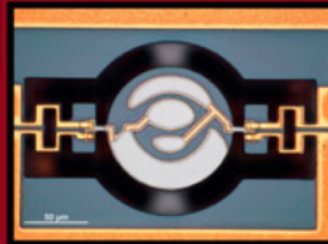
MEMS Phase Shifters



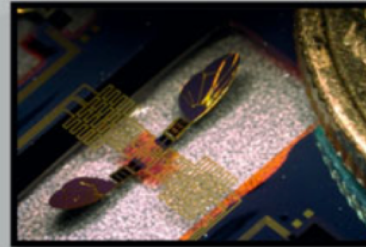
Mechanical Logic



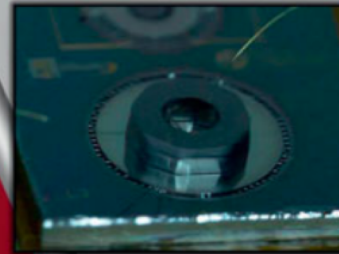
Resonators, Filters, & Transformers



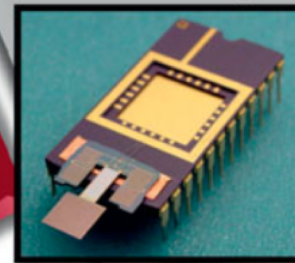
Micro-flight



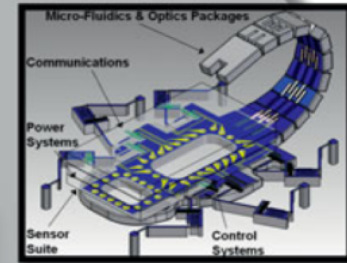
Ultrasonic Motor



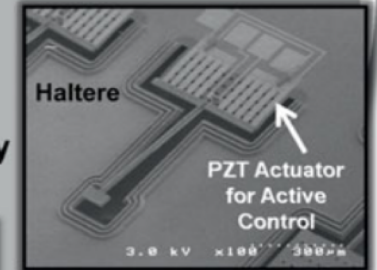
Piezoelectric Energy Harvesting



Terrestrial



Proprioceptive Sensors



MM-SCALE ROBOTICS

Figure 12. Montage of piezoelectric microelectromechanical (MEMS) devices. For the motor, the piezo MEMS stator is 3 mm in diameter, and the Si rotor is 2 mm in diameter. The switch uses a PZT actuator with a length of 125 microns. The phase shifter designed for 10 GHz operation has an overall dimension of 5.0 mm x 5.5 mm. The dual-wing micro wing structure was designed with 2 mm length wings. The piezoelectric energy harvester uses a 5-mm-long PZT thin-film cantilever that attached to a 5 mm x 5 mm proof mass. Image courtesy of Jeffrey S. Pulskamp and Ronald G. Polcawich, US Army Research Laboratory. Note: RF, radio frequency; PZT, Pb(Zr,Ti)O₃; CLK, clock; GND, ground.

Magnetron sputtering of ferroelectric thin film

- Target:
- Powder mixture, calcination in air 750C/3h, grounding + excess Bi₂=3:
Bi₂O₃,Nd₂O₃,Eu₂O₃,TiO₂
- Cu dish filled with powder, pressed with 40 Mpa
- Deposition at 650 C on conductive rutiel Nb(0.8w%):TiO₂ (101) substrate
- Sputter gas (Ar + ?) 0.1 – 5 Pa

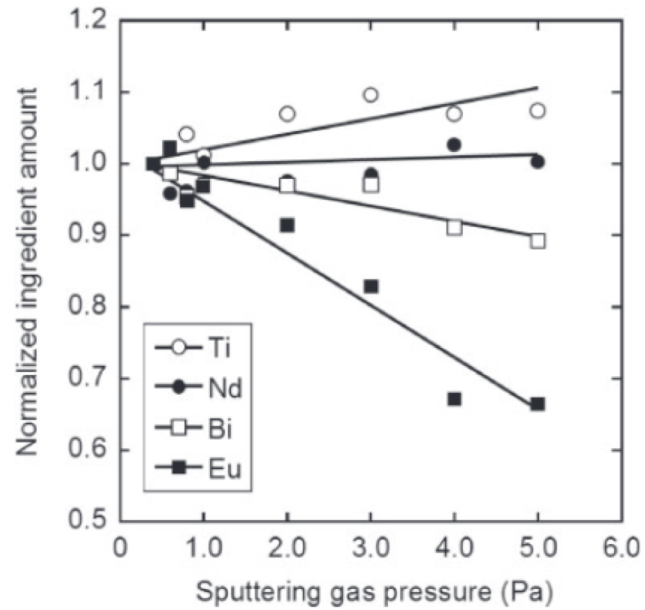


Fig. 3. Variation in film composition as a function of sputtering gas pressure. The Bi, Nd, Eu, and Ti contents were determined from the intensities of the Bi-M α peak at 2.42 keV, the Nd-L α peak at 5.23 keV, the Eu-L α peak at 5.85 keV, and the Ti-K α peak at 4.51 keV in the EDS spectra, respectively. All values are normalized by the value at 0.4 Pa for the corresponding element.

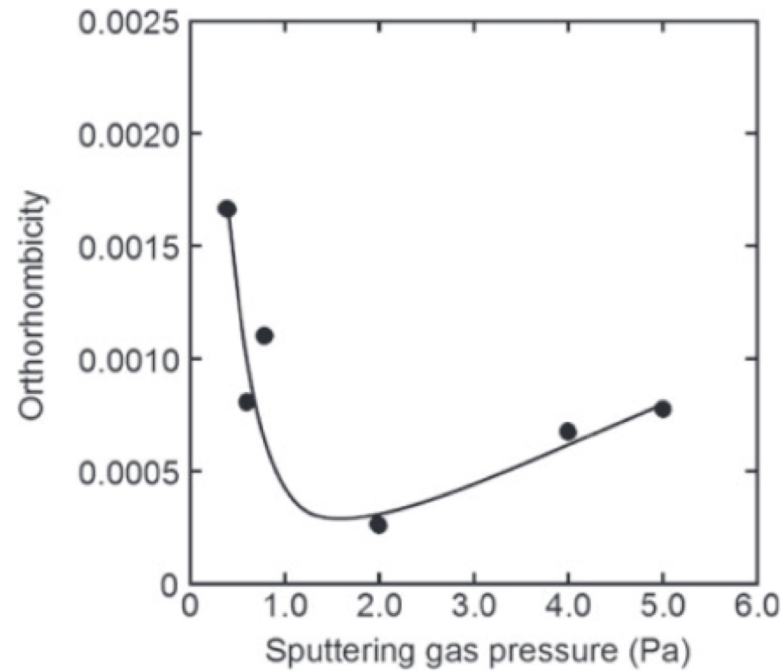


Fig. 4. Variation in room-temperature orthorhombicity of BNEuT-0.1 films as a function of sputtering gas pressure.

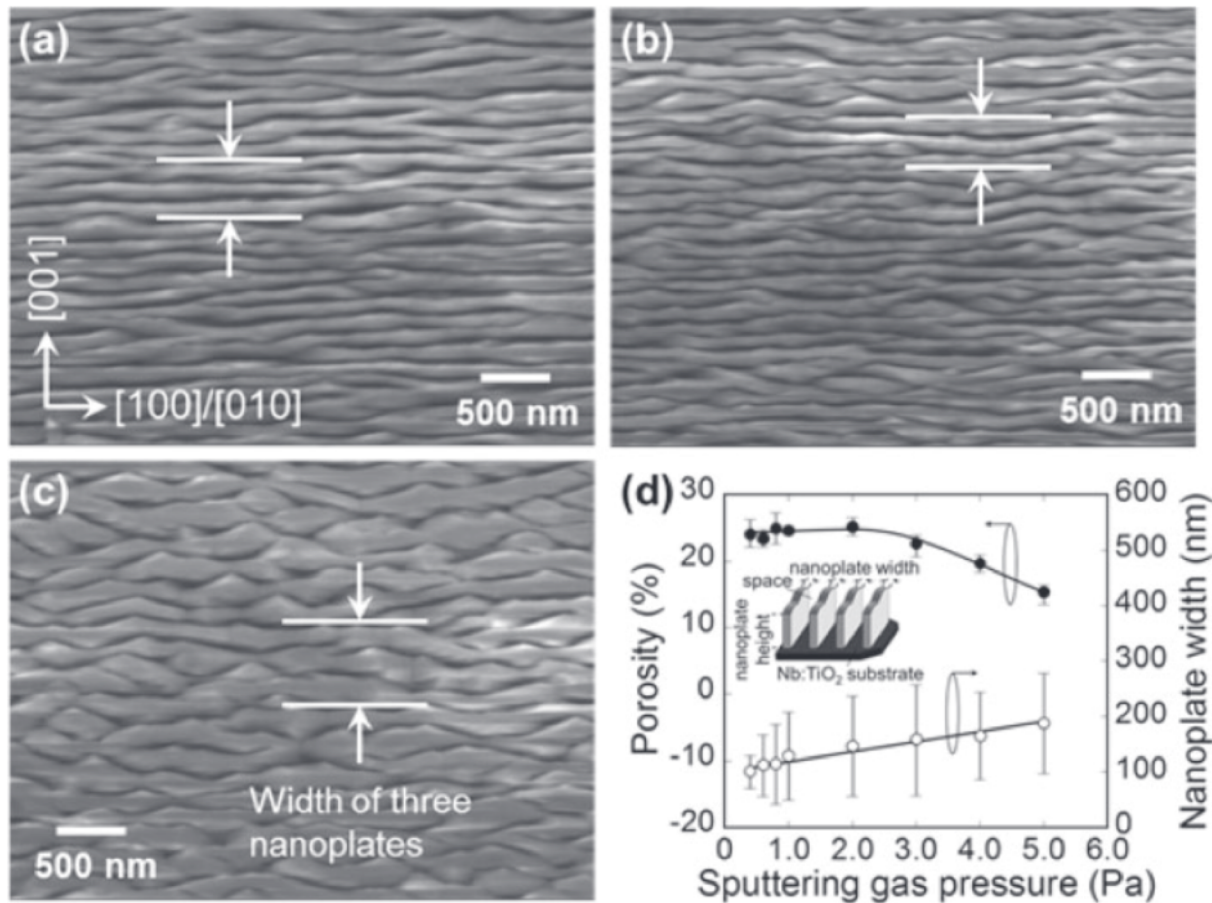


Fig. 5. Surface FE-SEM images of 1.8–2.3- μm -thick BNEuT-0.1 films deposited at (a) 0.4, (b) 1.0, and (c) 5.0 Pa, and (d) variation in nanoplate width along [001] direction as a function of sputtering gas pressure.

M. Kobune et al, Japanese Journal of Applied Physics 54, 10NA01 (2015)

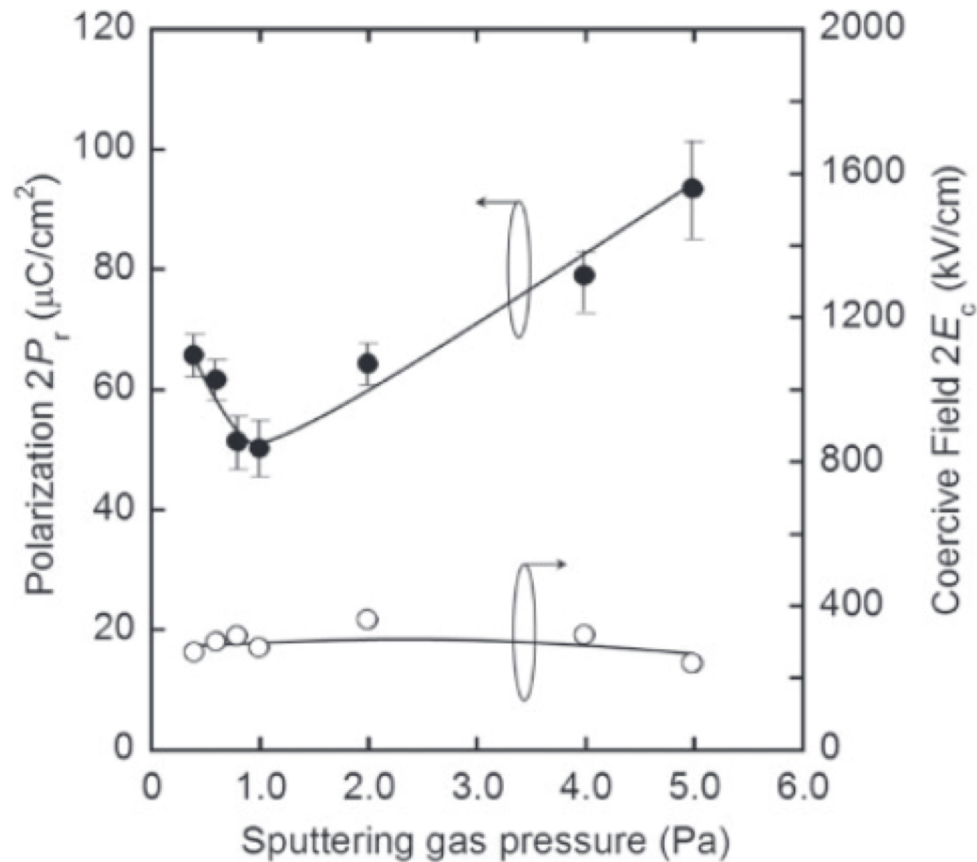
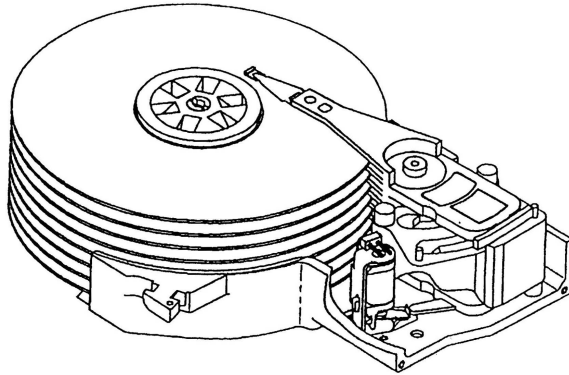


Fig. 7. Variations in room-temperature remanent polarization ($2P_r$) and coercive field ($2E_c$) for BNEuT-0.1 films with thicknesses of 1.8–2.3 μm as a function of sputtering gas pressure.

Ultra thin film protection of hard disks

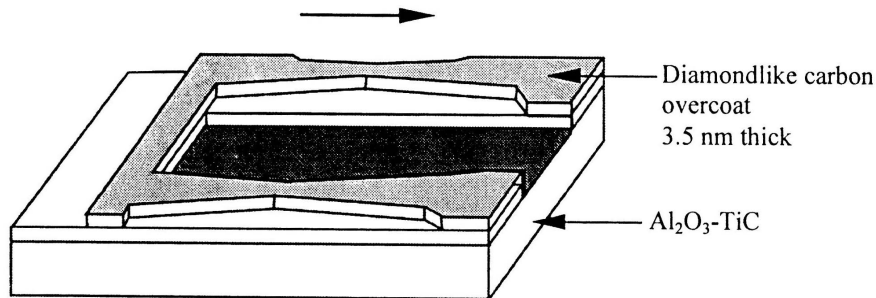
Magnetic rigid disc drive



Magnetic rigid-disk drive

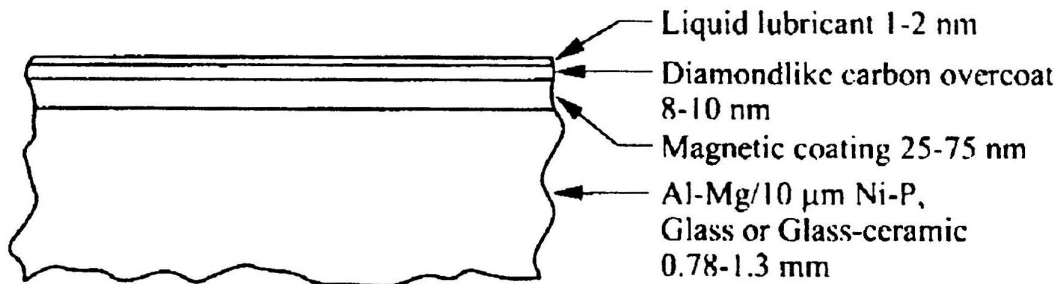
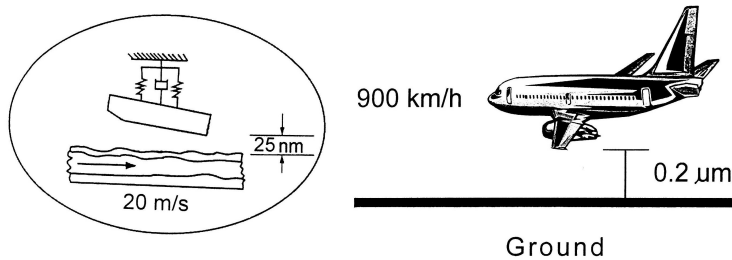
- A rigid disc drive consists of a stack of discs mounted on a spindle
- Disc stack is rotated at speed ranging from a few thousand to max. 15 000 rpm

A head slider is supplied for each disc surface.



MR type picoslider

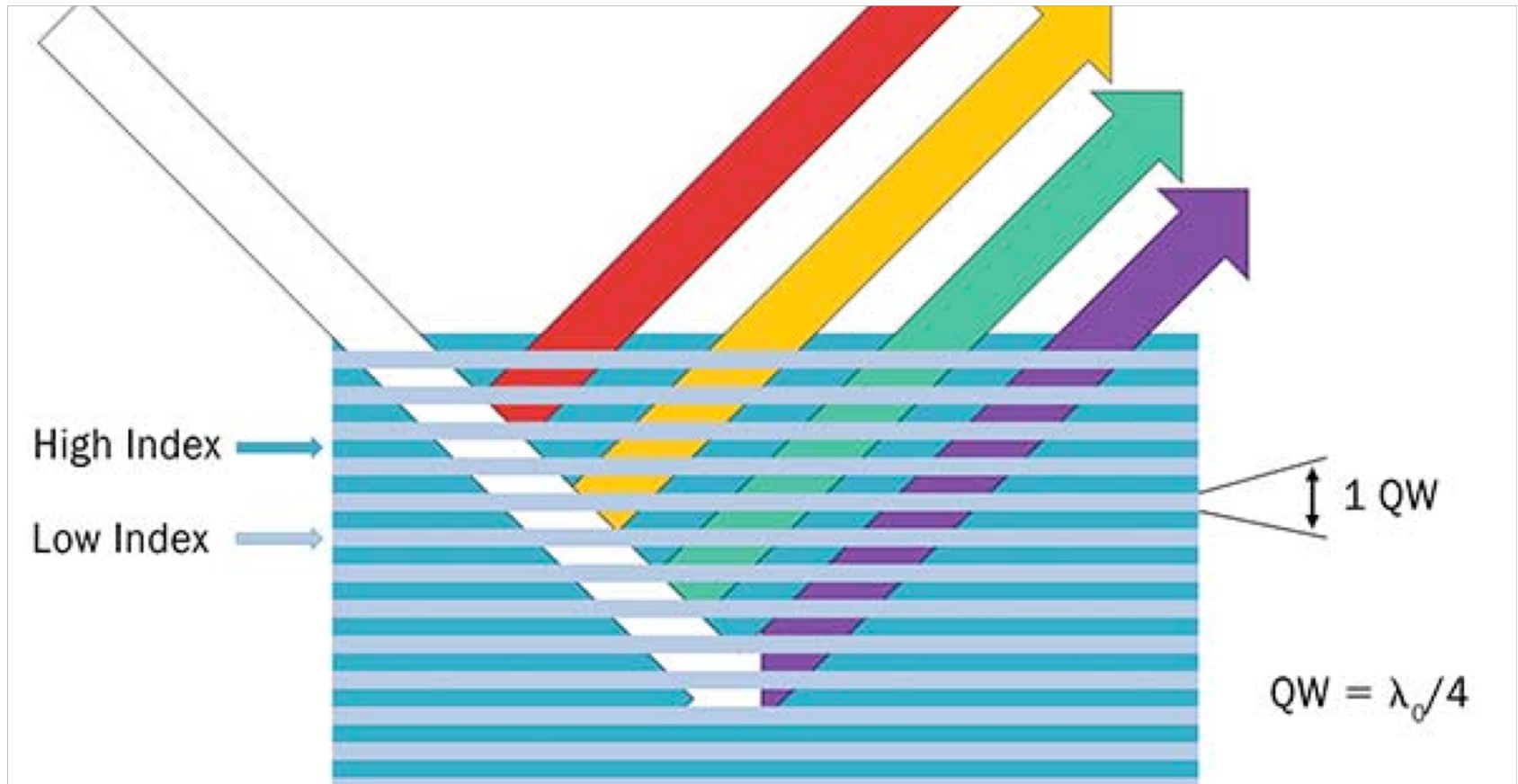
Magnetic rigid disc drive

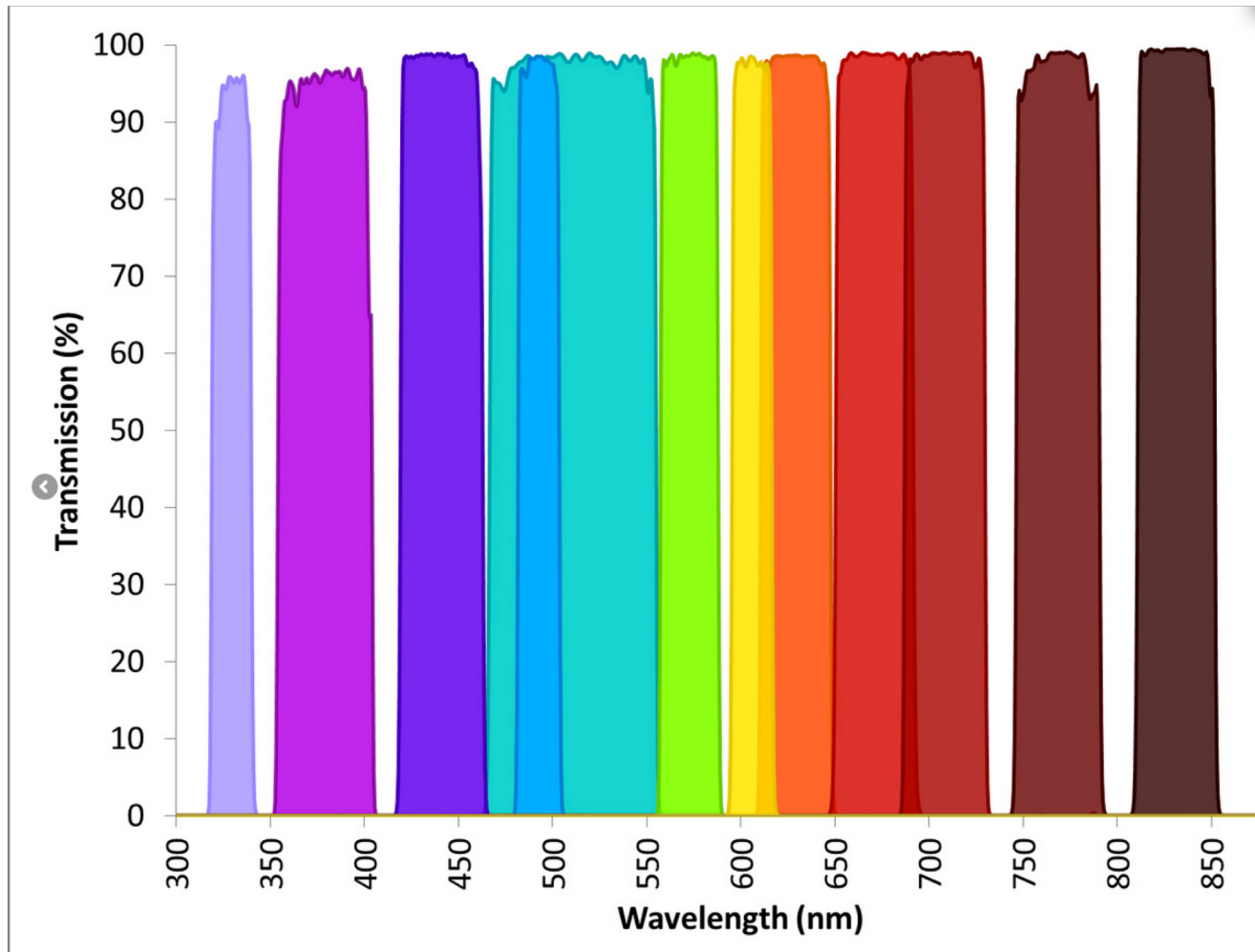


Thin-film disk

- Increasing high recording densities requires smooth surfaces and low flying heights
- In modern rigid disc drives flying height ranges from 20 to 50 nm and surface roughness from 1.5 to 5 nm RMS.

Optical thin film stacks





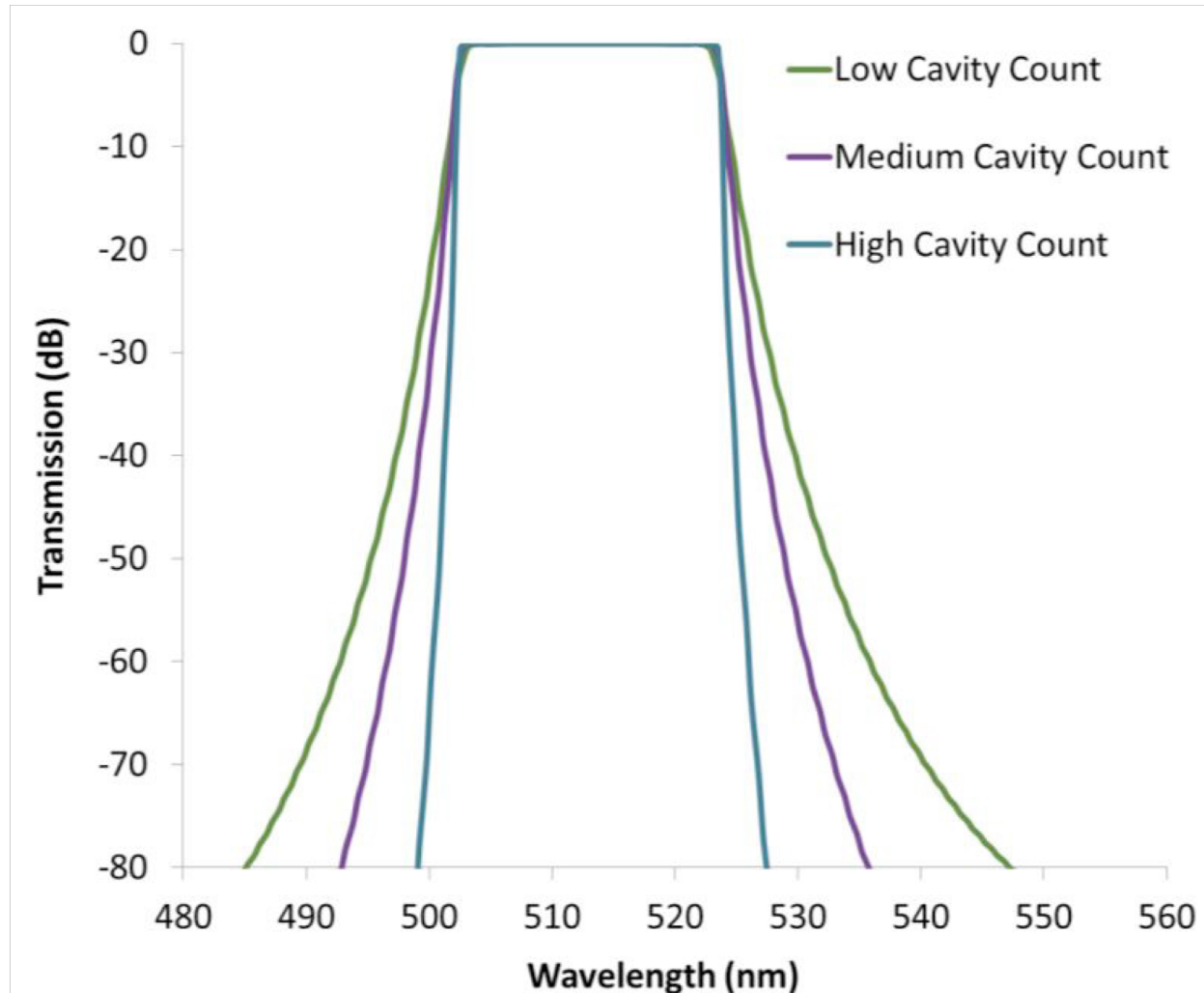


Figure 4. Filter “squareness” is a direct function of the number of resonant Fabry-Perot cavities in cavity filters, or the number of layers in LWP / SWP designs.

Deposition

- Evaporation
- Magnetron sputtering
- Ionbeam sputtering
- ALD

TABLE 2.
TYPICAL OPTICAL COATING MATERIALS CATEGORIZED BY SPECTRAL REGION AND REFRACTIVE INDEX INCLUDE PURE FORMULATIONS AND NOT MIXTURES

Wavelength Region (nm)	Low Index $n < 1.6$	Intermediate $n 1.6 - 1.8$	High Index $n \sim 2$
UV: 250 - 400	MgF ₂ , SiO ₂ , CeF ₃	Al ₂ O ₃ , Y ₂ O ₃	HfO ₂ , Sc ₂ O ₃
Visible - NIR: 400 - 1100	SiO ₂ , MgF ₂	Al ₂ O ₃ , Y ₂ O ₃	Ta ₂ O ₅ , Nb ₂ O ₅ , LaTiO ₃ , TiO ₂
UV: 250 - 400	MgF ₂ , SiO ₂ , CeF ₃	Al ₂ O ₃ , Y ₂ O ₃	HfO ₂ , Sc ₂ O ₃
SW - MWIR: 1100 - 5000	SiO ₂ , CeF ₃	Al ₂ O ₃ , Y ₂ O ₃ , SiO	Ta ₂ O ₅ , LaTiO ₃ , HfO ₂
LWIR: 5000 - 12,000	CeF ₃ , YF ₃ , ThF ₄	--	ZnS, ZnSe, Ge

Ph.D. Thesis

Thin films for gas sensors

José Miguel Alves Correia Pires*

27/11/2003

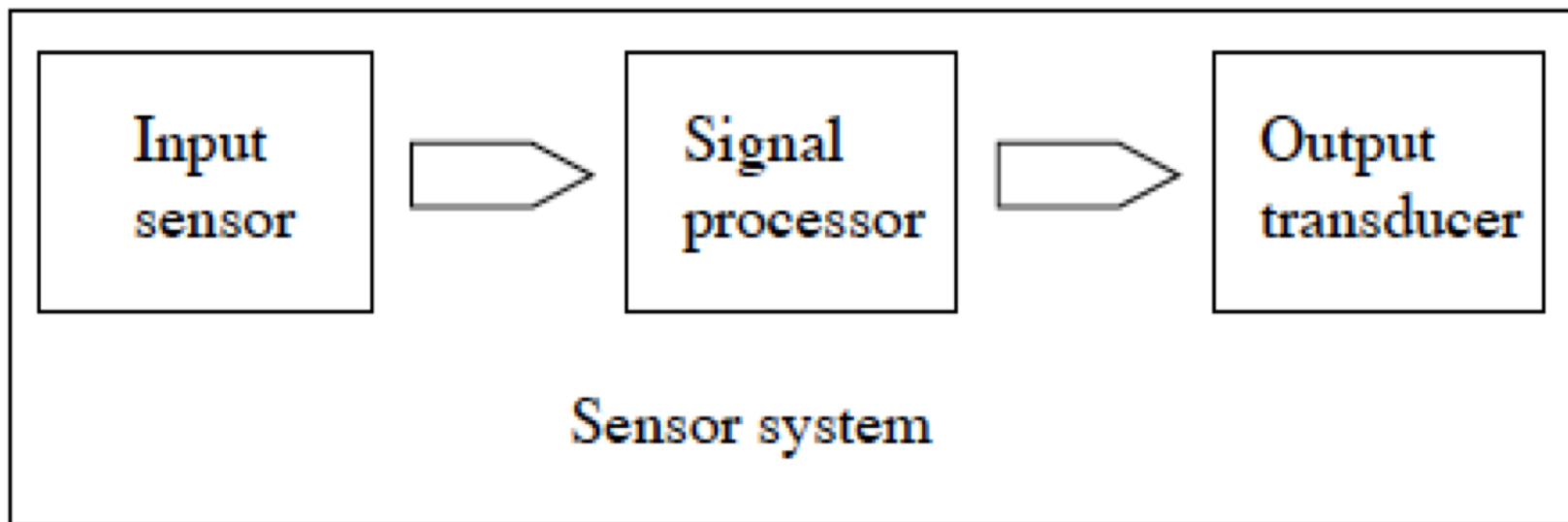
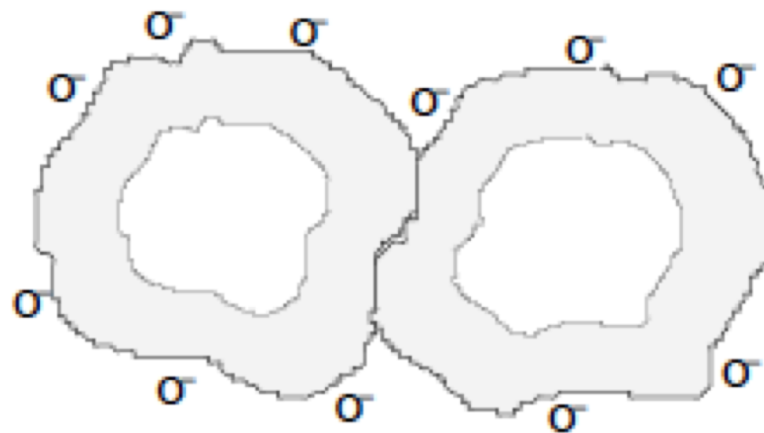


Figure 2.1.: Typical structure of a sensor system

Table 2.1.: Classification scheme based on the sensor' input stimulus

Class	Detected Properties
Mechanical	length, acceleration, flow, force, pressure, etc.
Thermal	temperature, specific heat, heat flow, etc.
Electrical	charge, current, voltage, resistance, inductance, etc.
Magnetic	magnetic flux density, magnetic moment, etc.
Optical	light intensity, wavelength, polarization, etc.
Radiation	type, number or energy of radiation particles; light properties far from the visible spectrum; etc.
Chemical	composition, concentration, pH, etc.



(a) in air



(b) with CO

Figure 6.8.: Grain contact model and barrier control scheme

Table 4.1.: Range of parameters selected for DC and RF sputtering deposition of tin oxide samples

Parameter	DC sputtering	RF sputtering
Temperature (° C)	60–400	40–400
Source power (W)	—	200–800
Source current (A)	0.08–0.30	—
Pressure ($\times 10^{-1}$ Pa)	.25–12	4–10
O ₂ flow rate (sccm)	3.6–14.8	25–50
Substrate-target distance (mm)	55–76	60–80
Sputtering time (min)	5–120	5–120
Pre-sputtering time (min)	2–27	0–10
Etching power (W)	—	100, 200
Etching time (min)	—	0, 10
Power applied to substrate bias (W)	—	0–50

Table 4.2.: Non-independent parameters controlled during deposition

Parameter	DC sputtering	RF sputtering
Target voltage (V)	200–350	—
Ar flow rate (sccm)	5.4–26	67–160
O ₂ partial pressure ($\times 10^{-1}$ Pa)	.13–.65	4–10

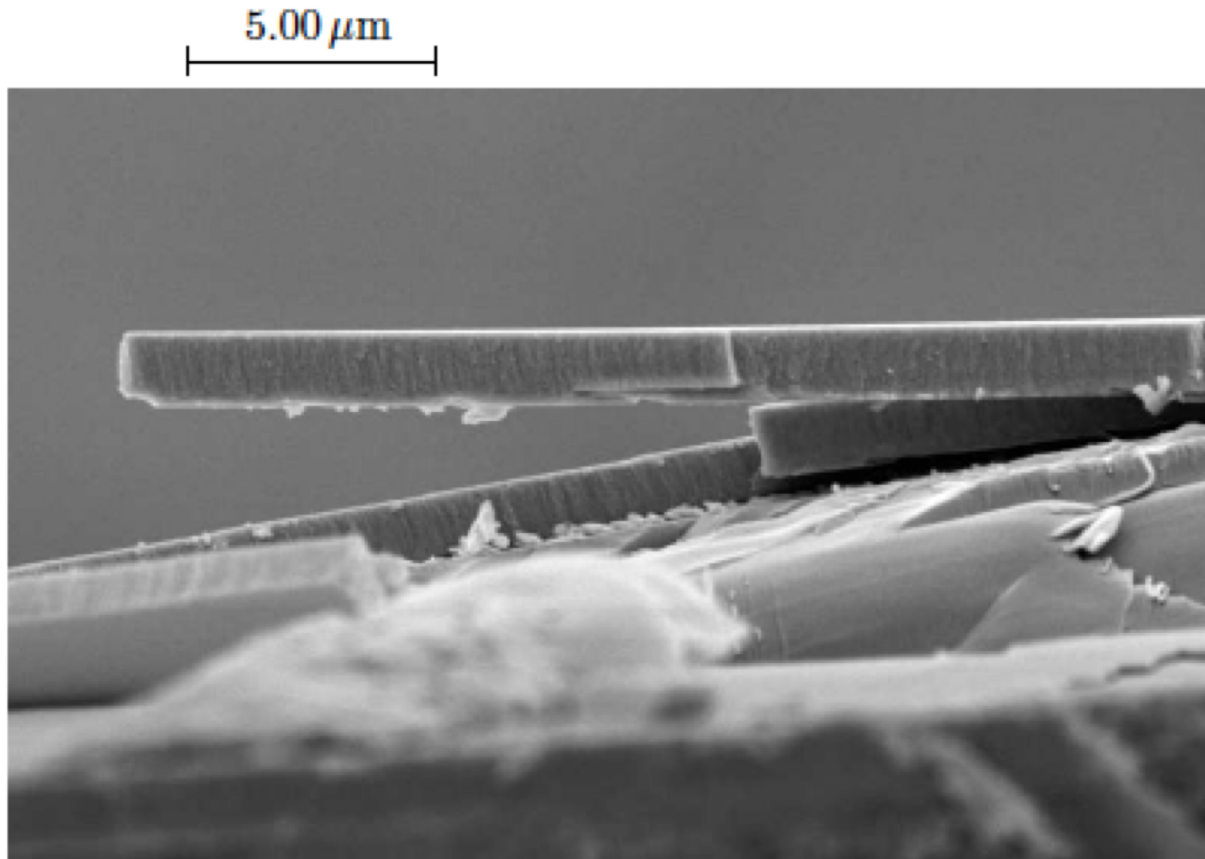


Figure 4.6.: SEM image showing delamination of a SnO₂ layer

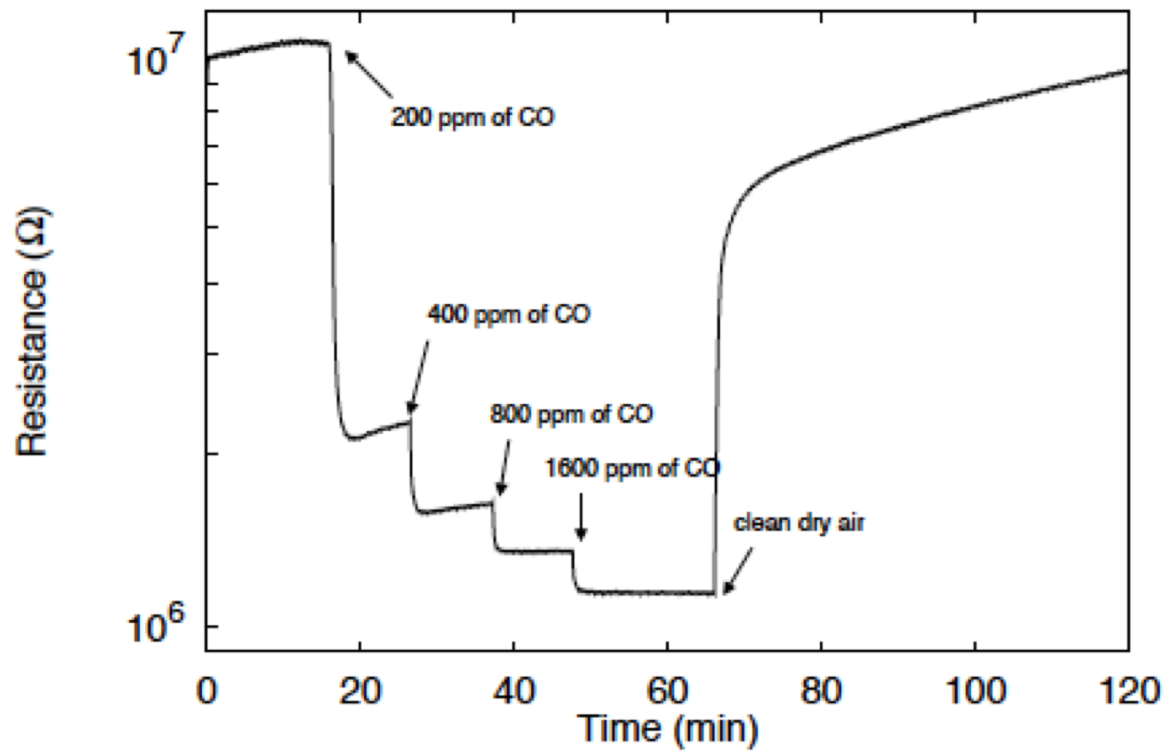
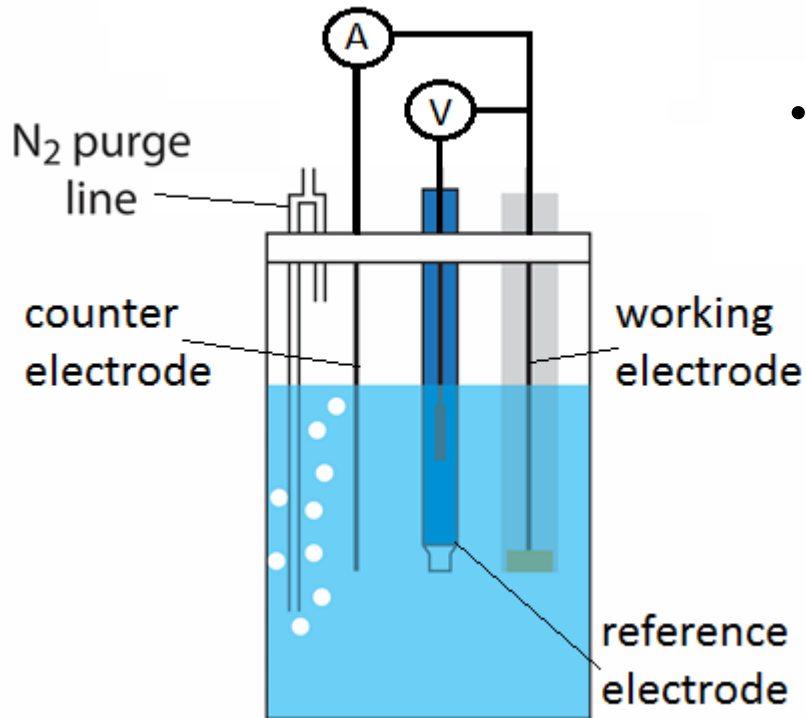


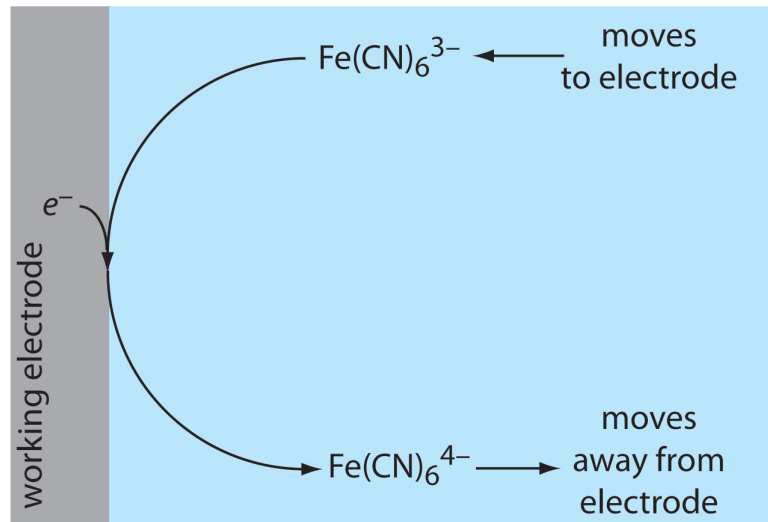
Figure 6.17.: Sample response to concentrations of carbon monoxide between 100 ppm and

Bio molecular sensing

3 Electrode electrochemical measurement: Ferrocyanide reduction



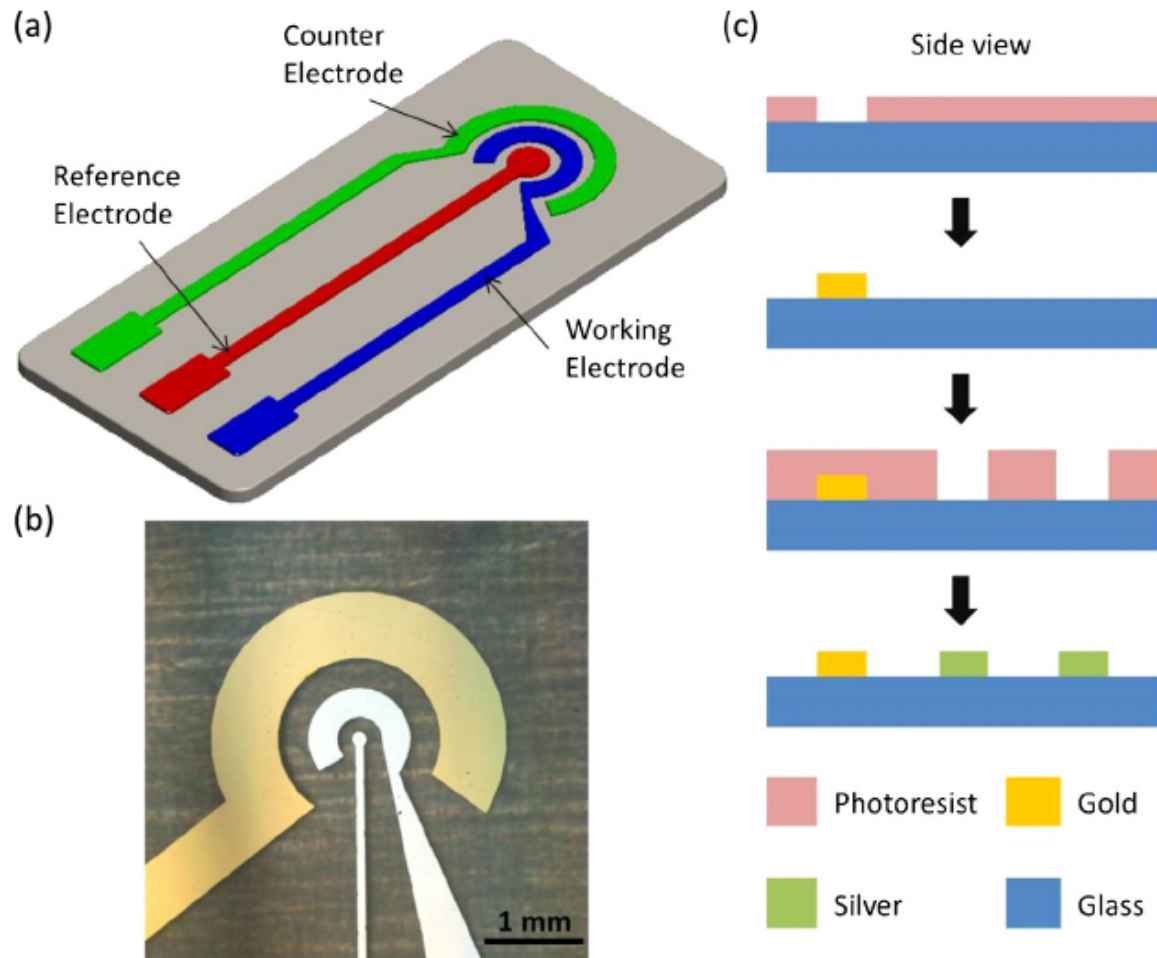
- Potential: between working and reference electrode
- Current measured between working and counter electrode



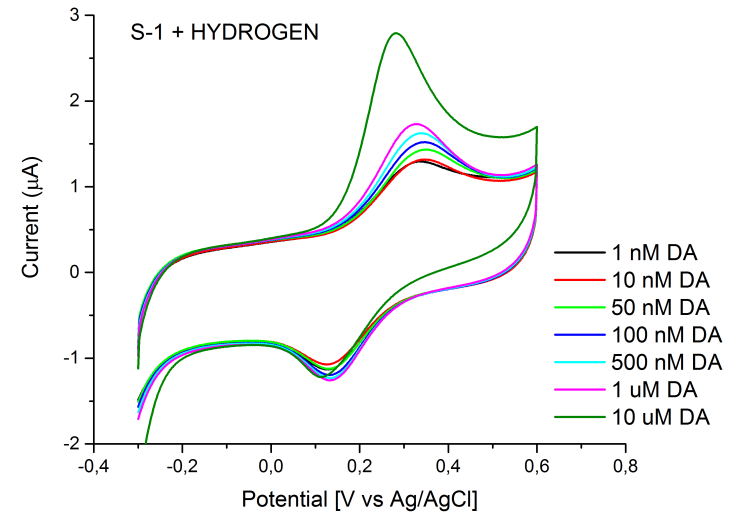
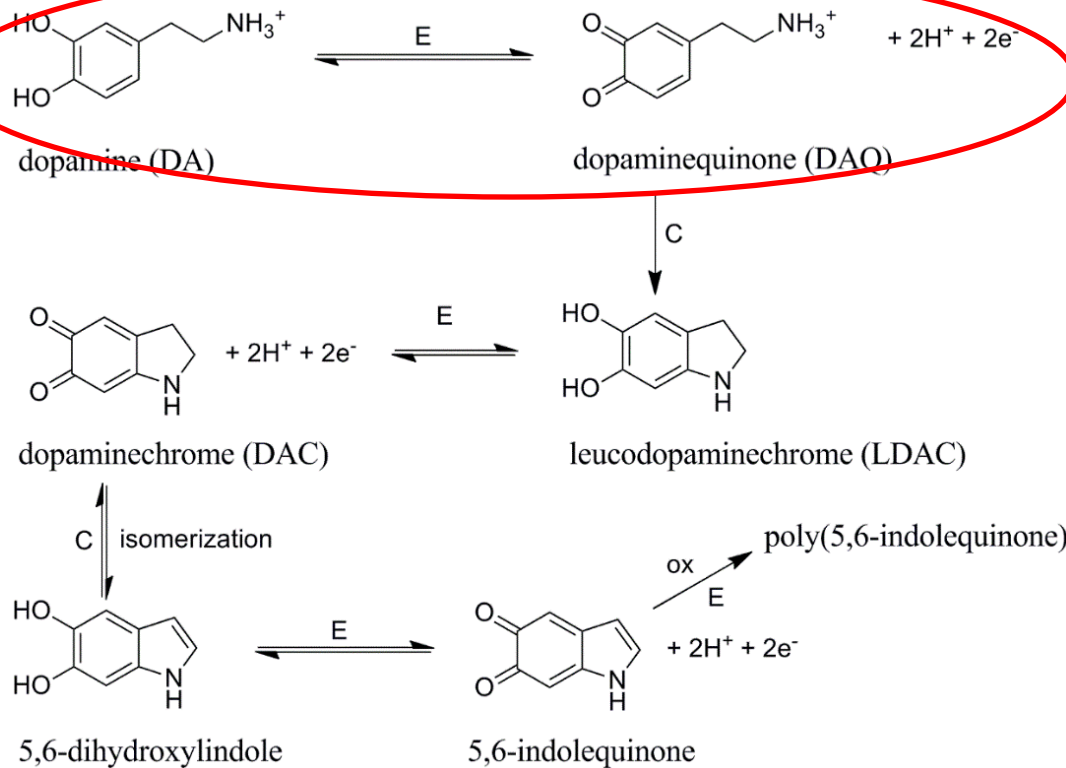
[chem.libretexts.org/Textbook_Maps/Analytical_Chemistry_Textbook_Maps/Map%3A_Analytical_Chemistry_2.0_\(Harvey\)/11_Electrochemical_Methods/11.4%3A_Voltammetric_Methods](http://chem.libretexts.org/Textbook_Maps/Analytical_Chemistry_Textbook_Maps/Map%3A_Analytical_Chemistry_2.0_(Harvey)/11_Electrochemical_Methods/11.4%3A_Voltammetric_Methods)

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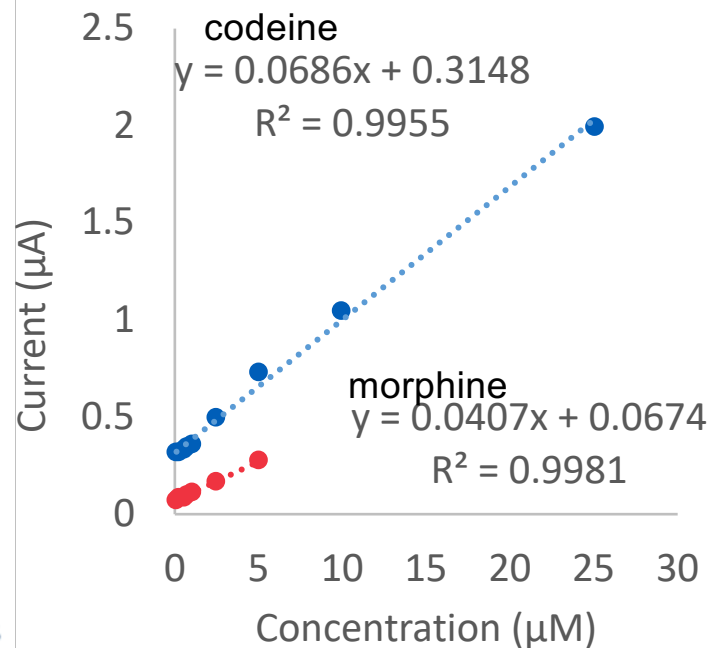
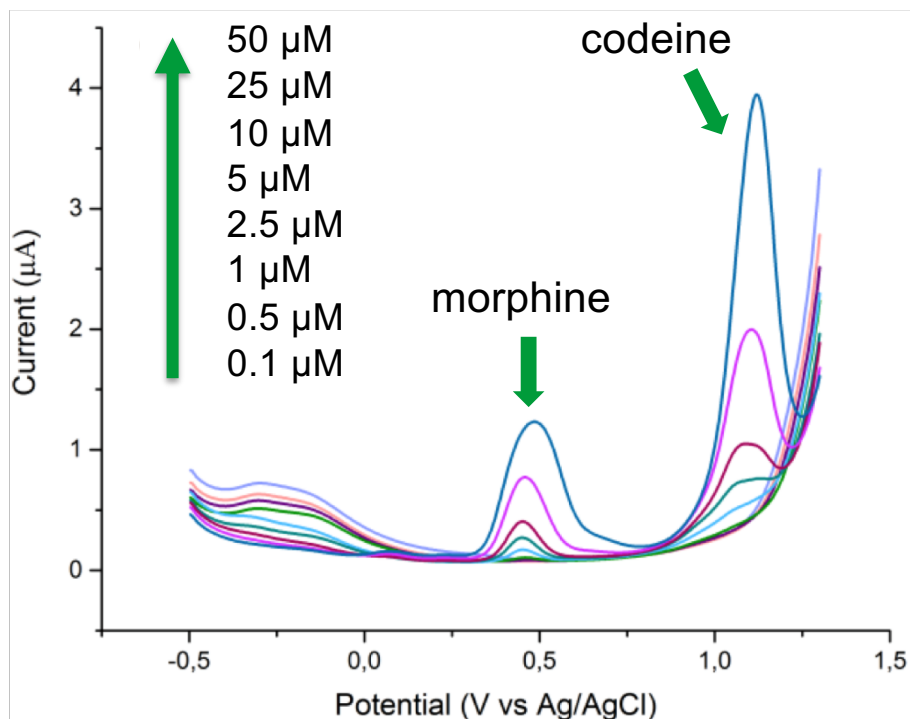
Integrated thin film 3-electrode test strip



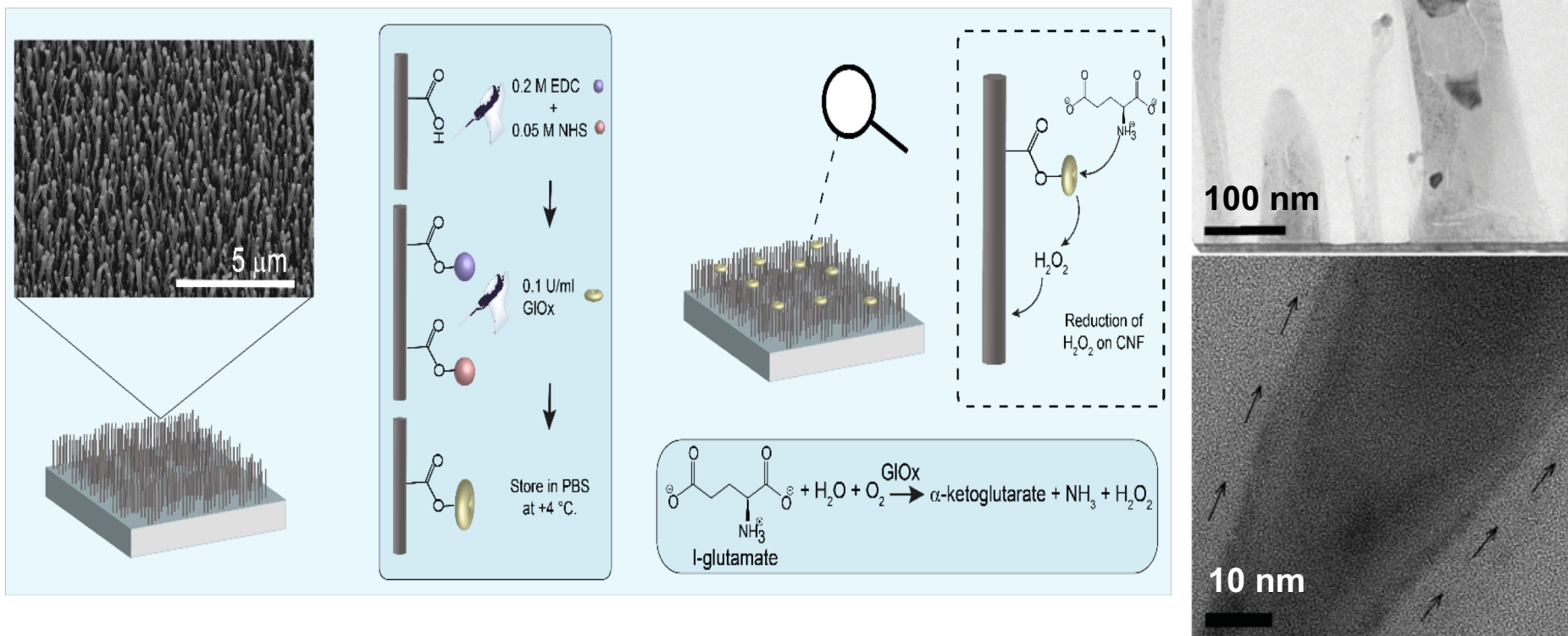
Electrochemical detection of Dopamine (DA)



Detection of Morphine and codeine

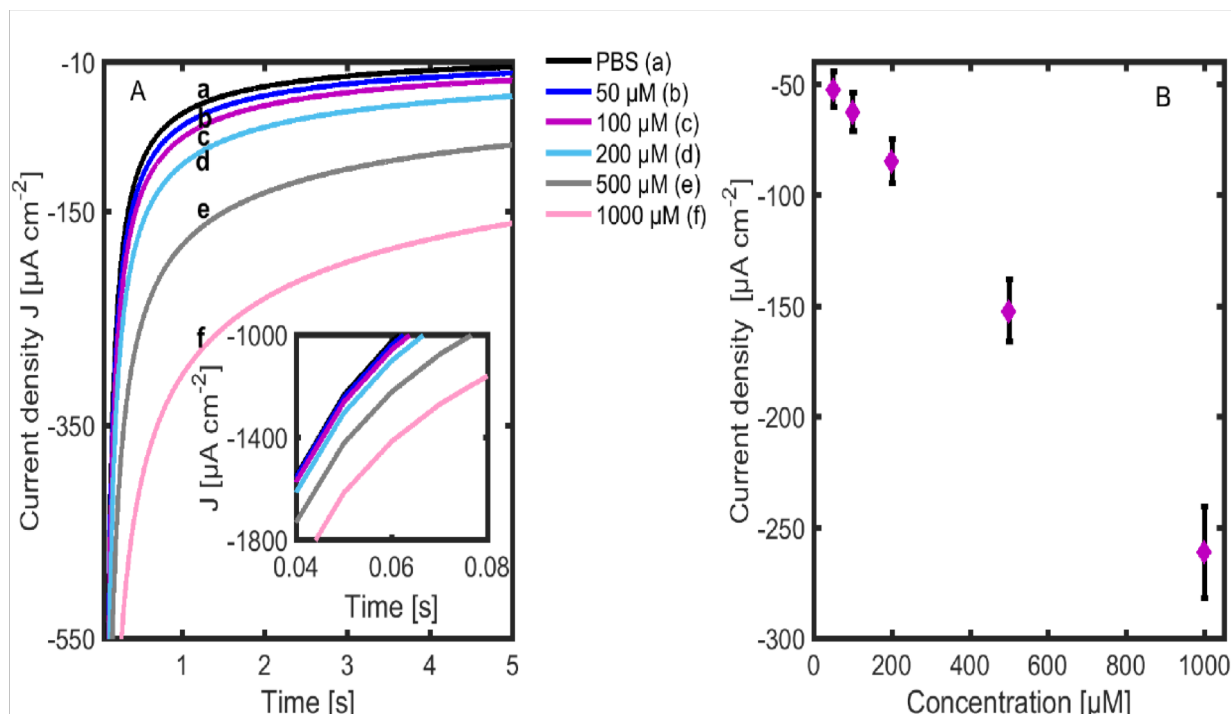


CNF for enzymatic detection of Glutamate

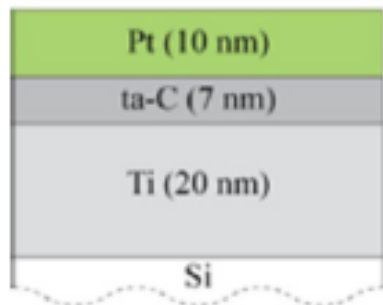


CNF for enzymatic detection of Glutamate

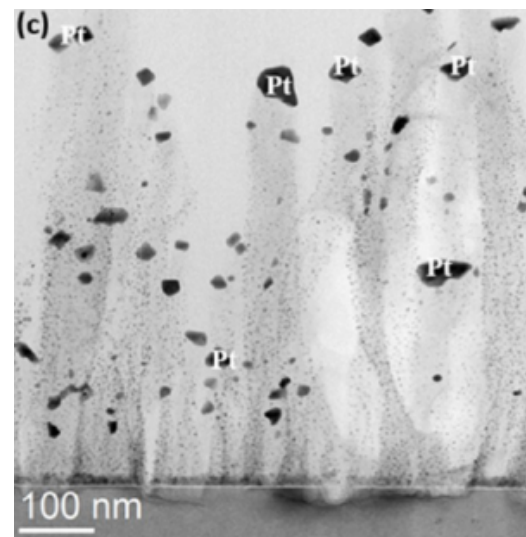
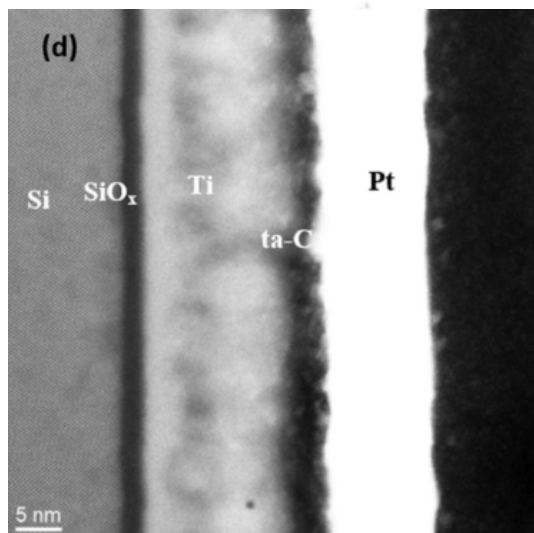
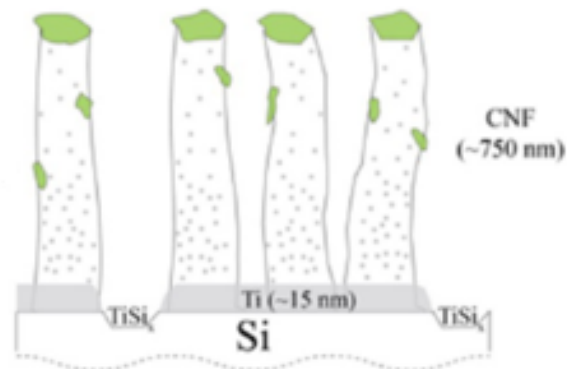
Detection of H_2O_2 , Reaction product of enzymatic oxidation



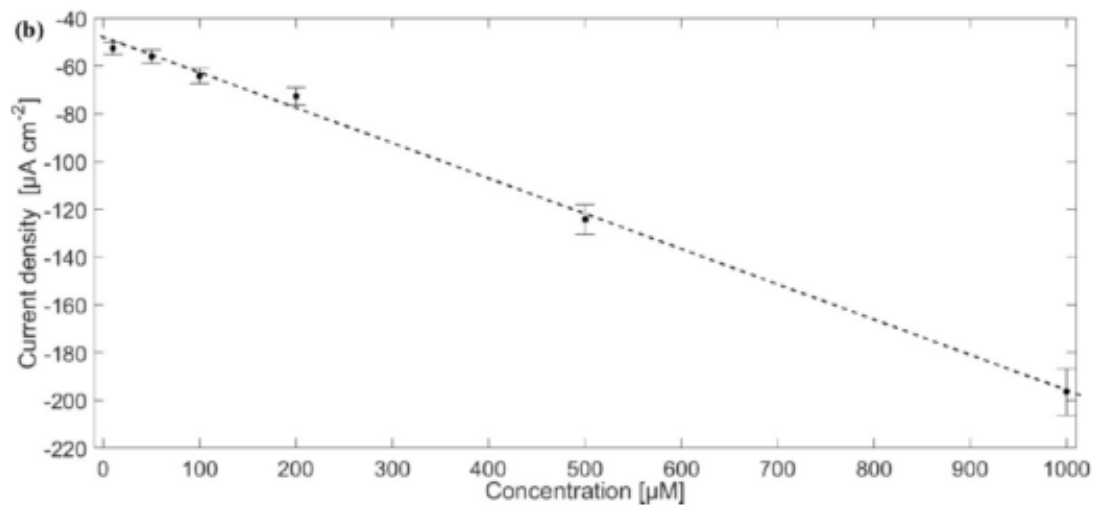
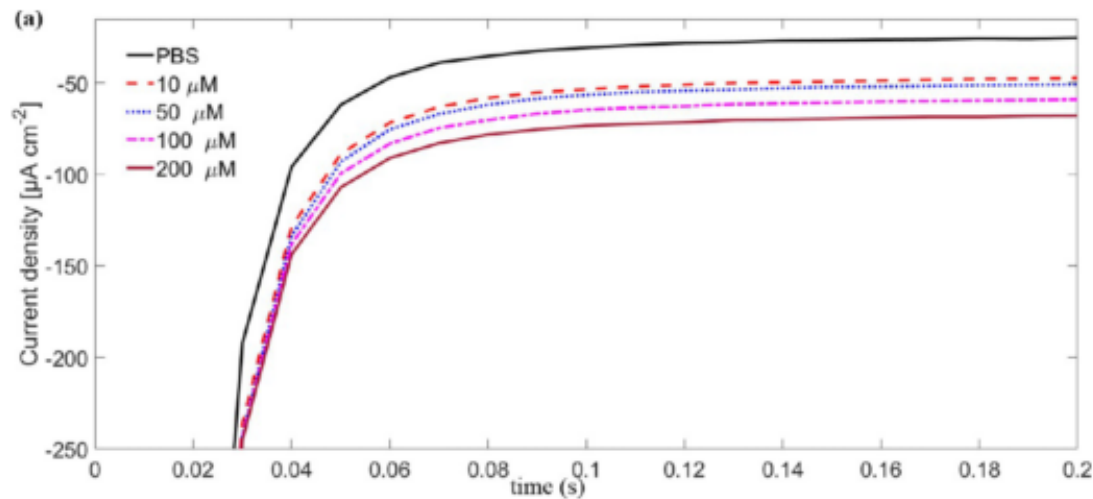
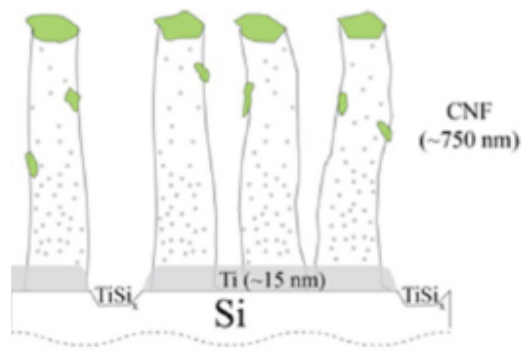
Pt-CNF for enzymatic detection of Glutamate



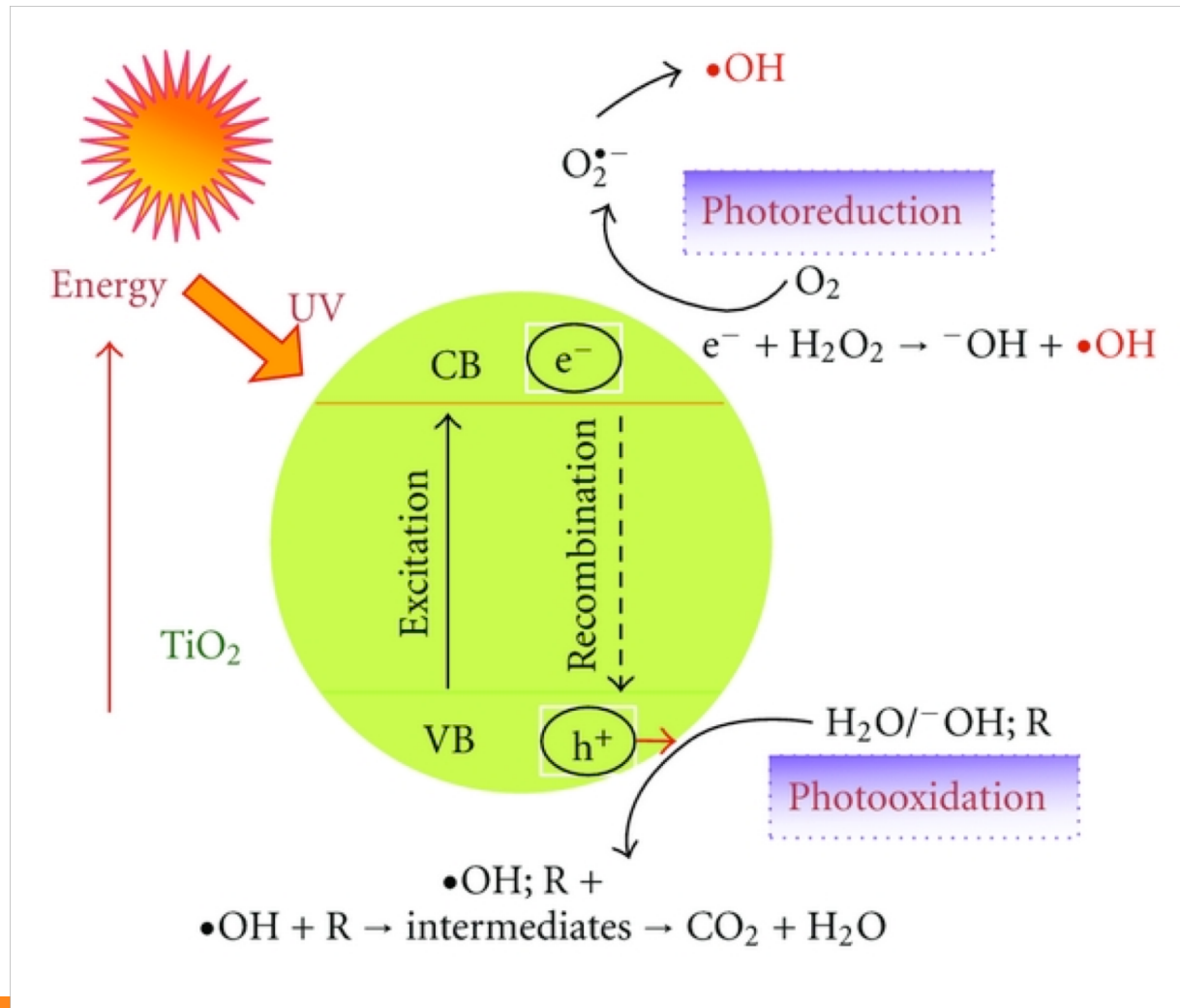
PECVD
With
 $\text{NH}_3 + \text{C}_2\text{H}_2$

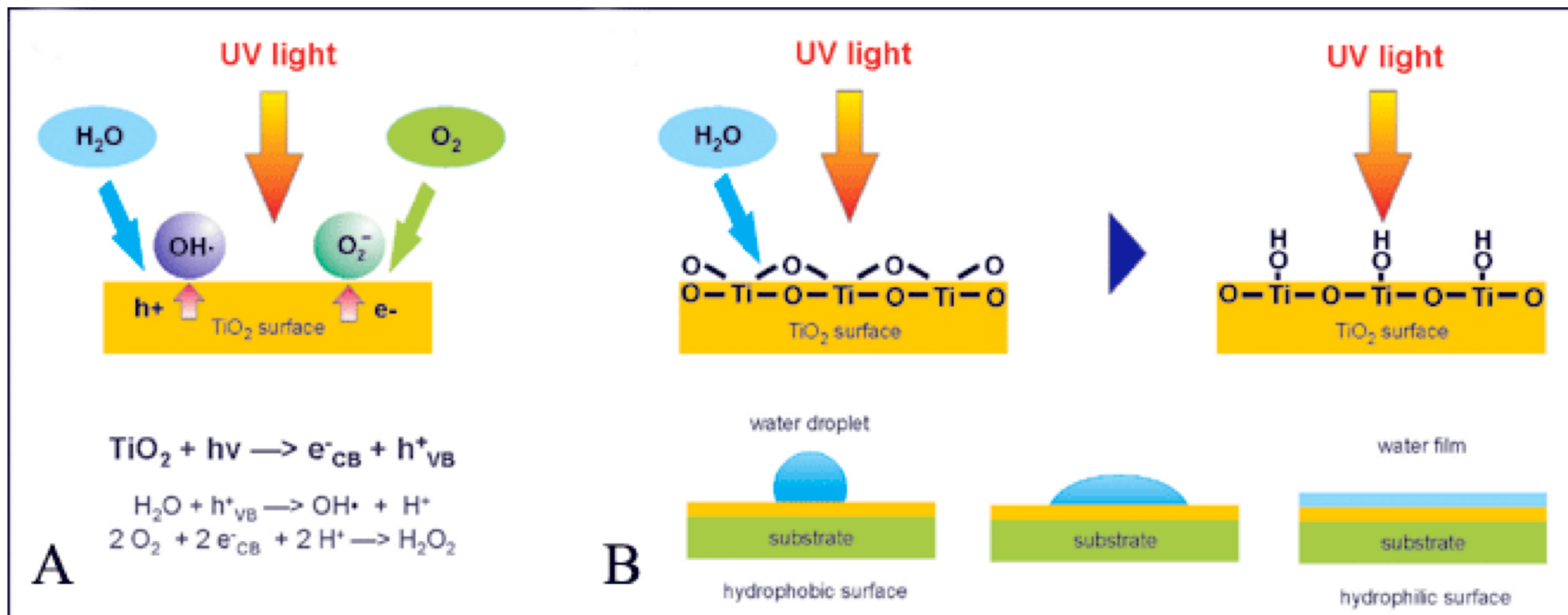


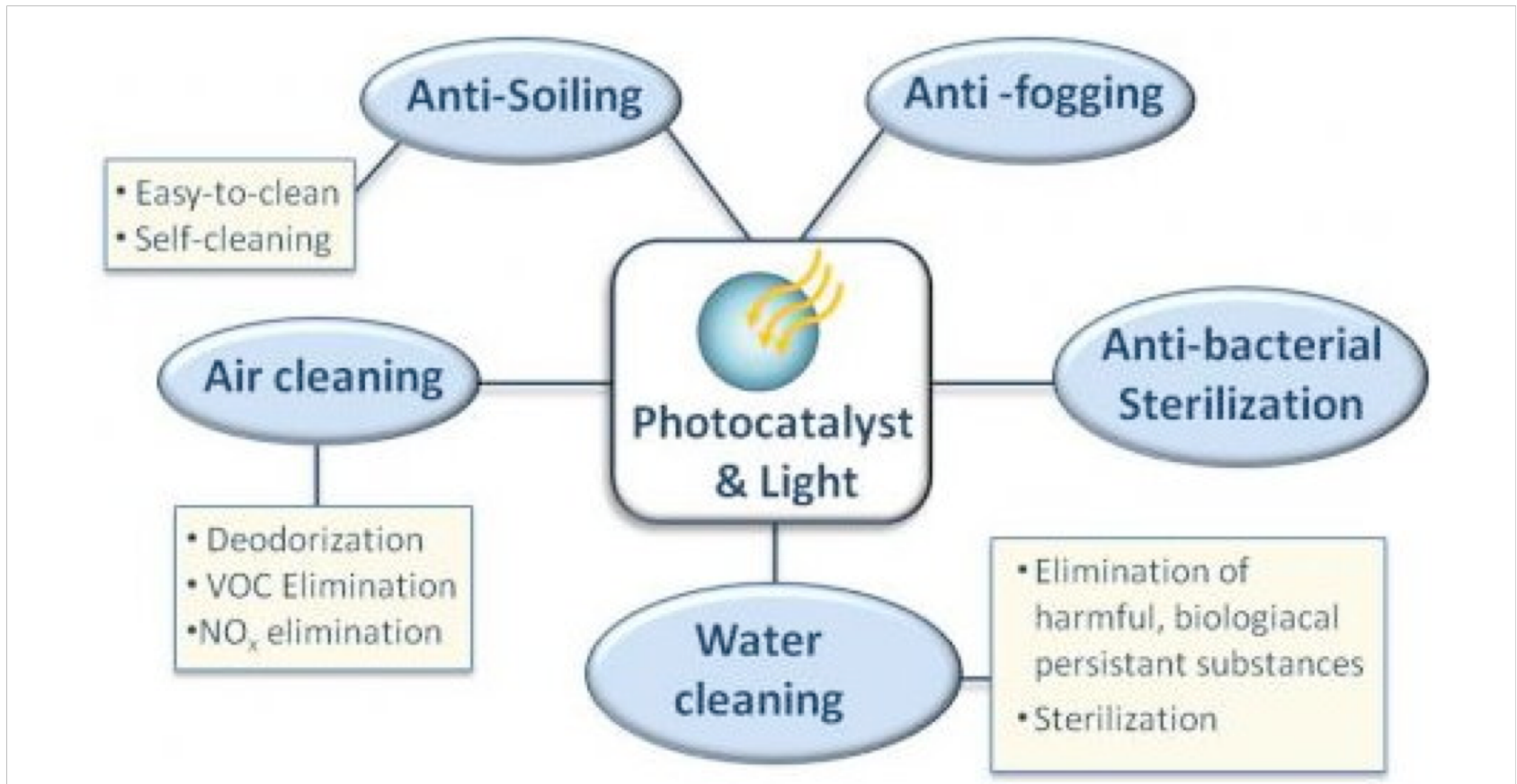
Pt-CNF for enzymatic detection of Glutamate

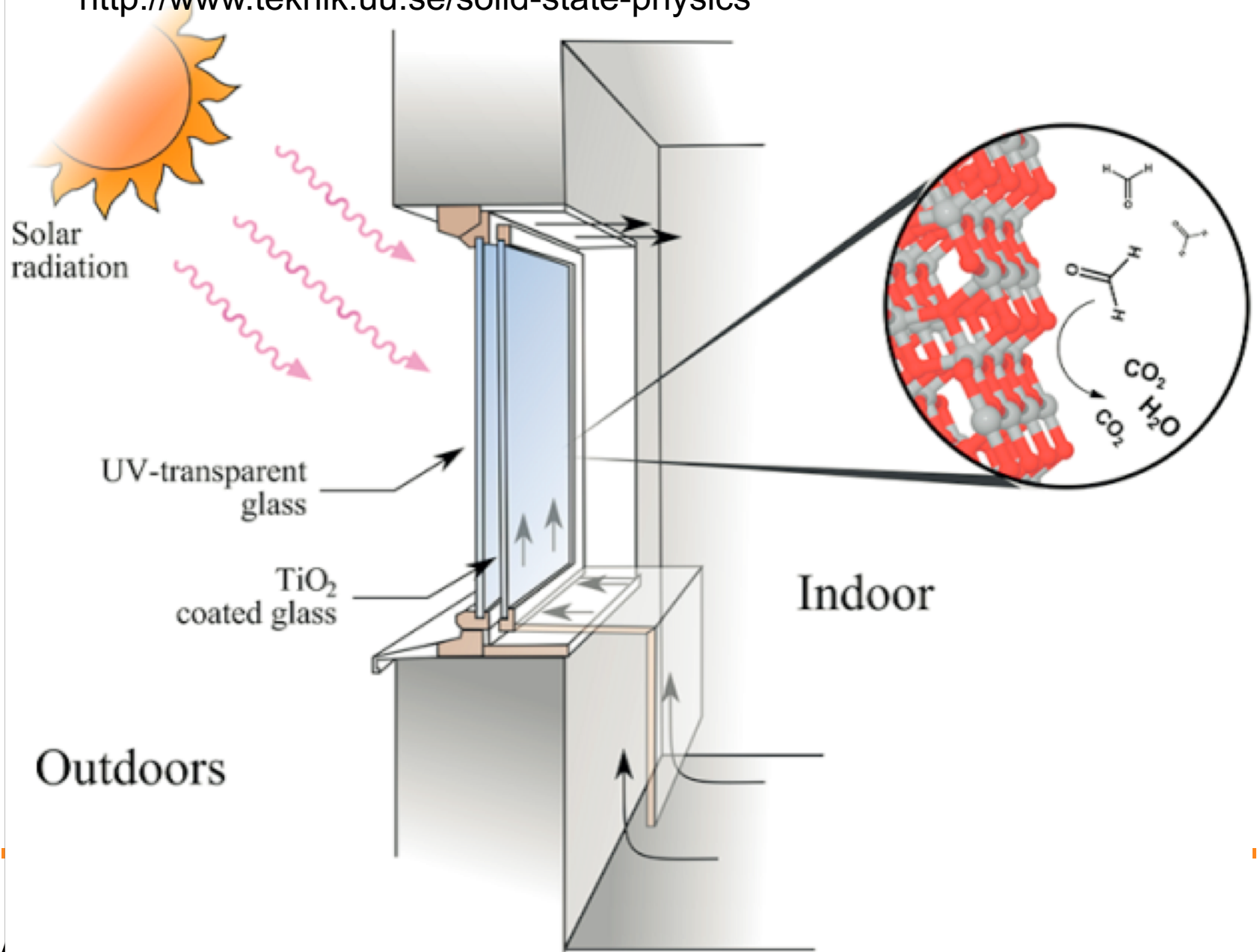


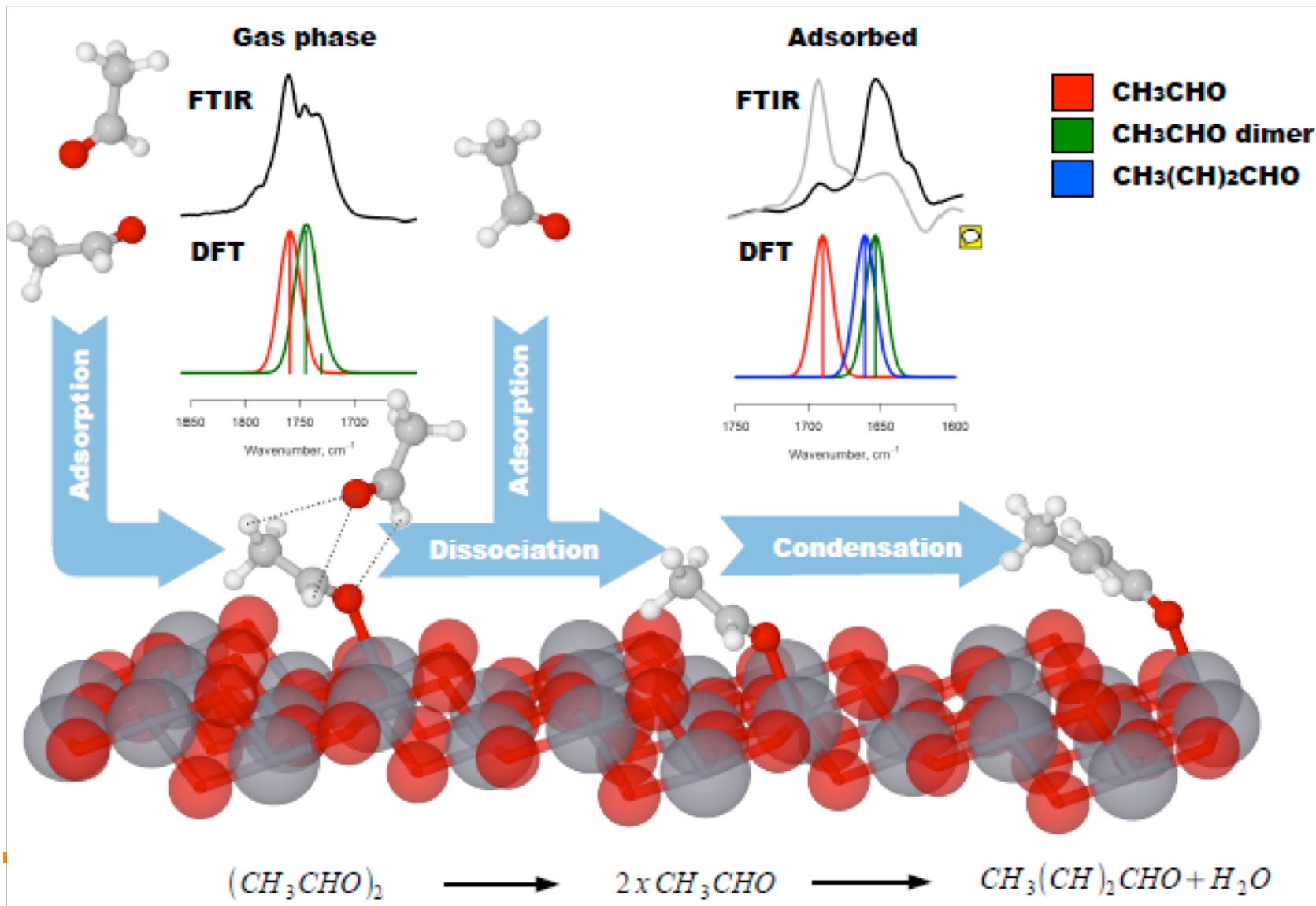
Photocatalytic TiO₂ films









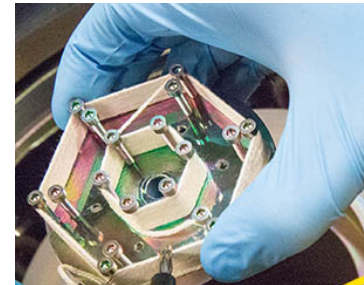
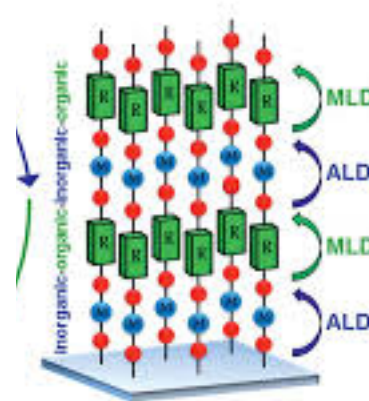
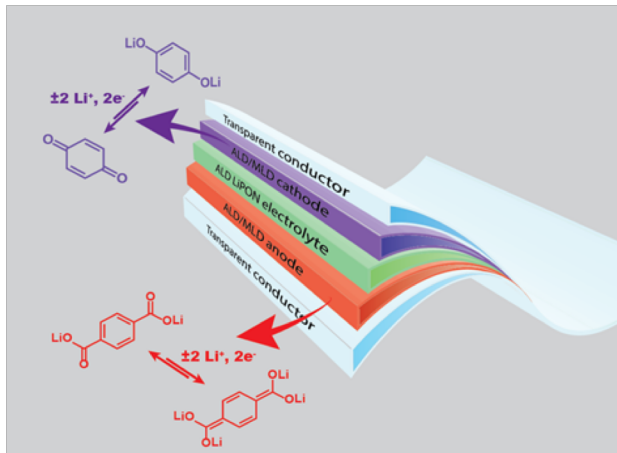


Batteries

IoT, MEMS, CMOS memories, Medical implantable	Smart cards, Skin patch, RFID	Wearables, E-textile, Medical device	Smartphone, Tablet, Power tool, Toy	Transport	Large-scale energy storage
Capacity range →					
1 mAh	10 mAh	100 mAh	1 Ah	100 Ah	> 1 kWh
Important features					
<ul style="list-style-type: none"> • Rechargeable • Small footprint, many micro-batteries • Long life time • Rapid discharge • Tend to incorporate with energy harvesting 	<ul style="list-style-type: none"> • Can be both disposable and rechargeable • Laminar and thin, some with special form factor • Relatively low power • Cost sensitive 	<ul style="list-style-type: none"> • High energy density for small volume • Long working hours • Flexible, stretchable or thin, some with special form factor 	<ul style="list-style-type: none"> • Light-weight and small volume • Long working hours • Some with special form factors • High power 	<ul style="list-style-type: none"> • Safe • Reliable • High power • High capacity 	<ul style="list-style-type: none"> • Cost advantage • Long life time • Reliable • High capacity
					
Technology Status					
Small volume production	Available, mostly customized	Prototypes available	Research to prototype	Research	Very early stage

Wearable electronics by ALD

- Prof. Maarit Karppinen group



And numerous other functional thin films

- Bio-active, bio compatible
- Controlled (drug) release
- Stimulus-responsive
- Magnetostrictive
- Piezoresistive
- etc.