

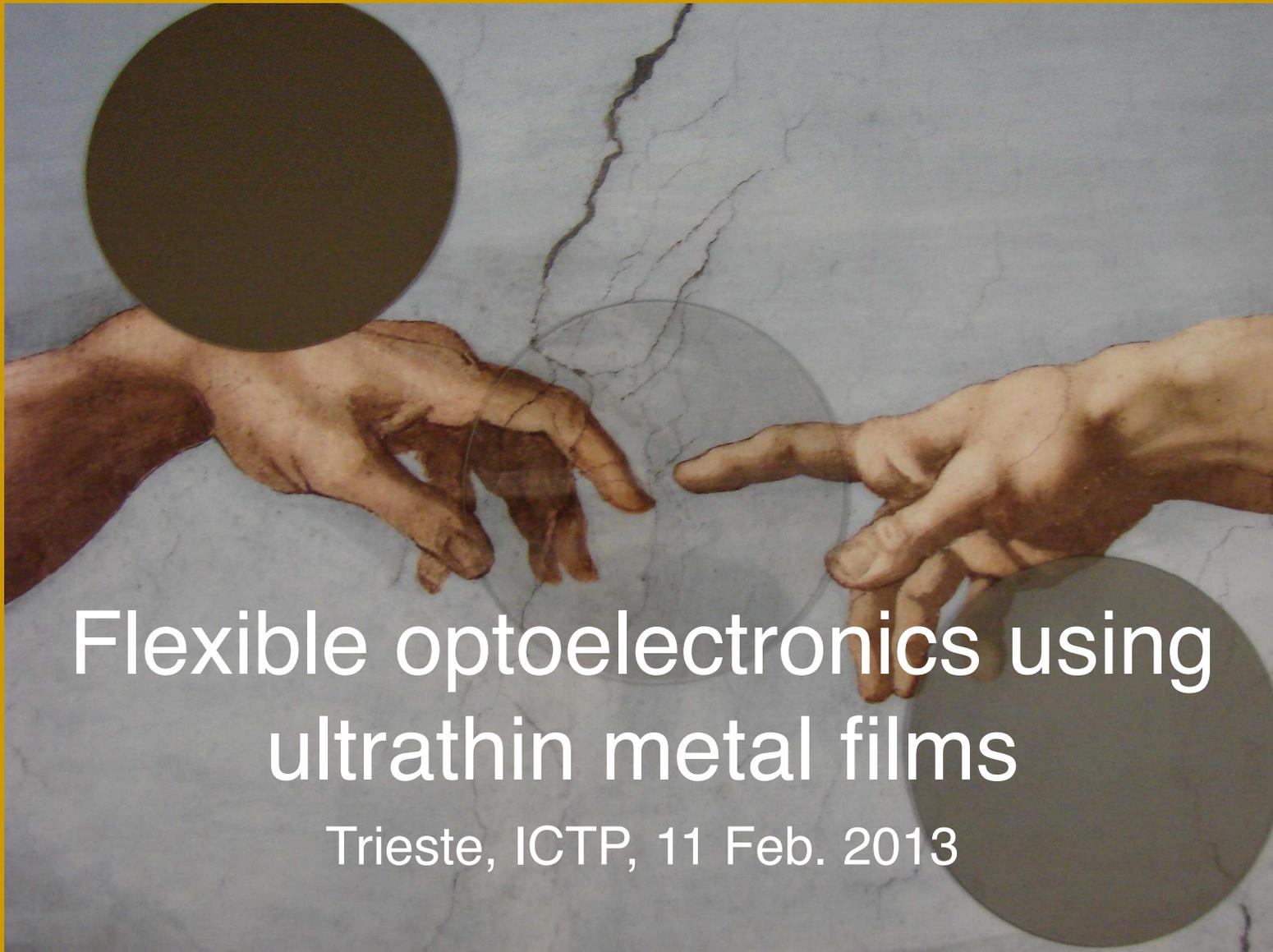
2443-21

**Winter College on Optics: Trends in Laser Development and Multidisciplinary
Applications to Science and Industry**

4 - 15 February 2013

Flexible optoelectronics using ultrathin metal films

V. Pruneri
*ICFO
Spain*



Flexible optoelectronics using ultrathin metal films

Trieste, ICTP, 11 Feb. 2013

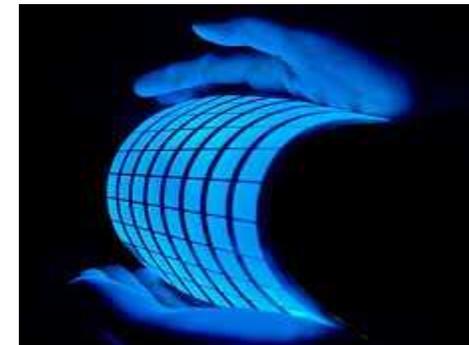
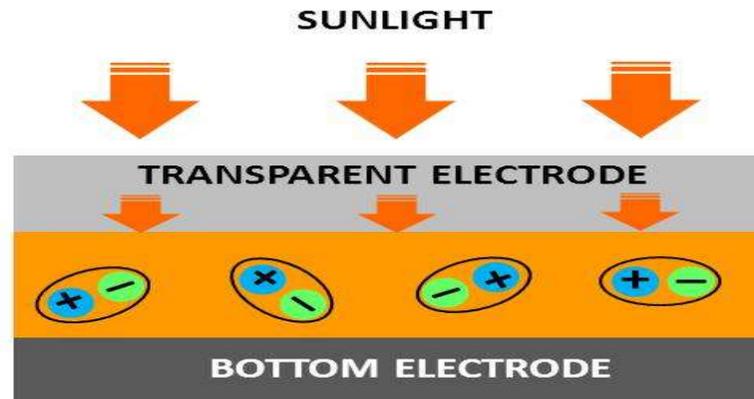
Outline

2

- ❑ Market, applications and requirements for transparent electrodes (TEs)
- ❑ Basics of ultrathin metal films (UTMFs) – broadband transparency
- ❑ New TE geometries
 - ❑ UTMF Multilayer
 - ❑ Combination of UTMF and Al:ZnO
 - ❑ Enhancement using conductive grid
- ❑ Incorporation in 3-D, heads-up displays, OLEDs and OSCs
- ❑ Use to create nanostructured surfaces
- ❑ Graphene

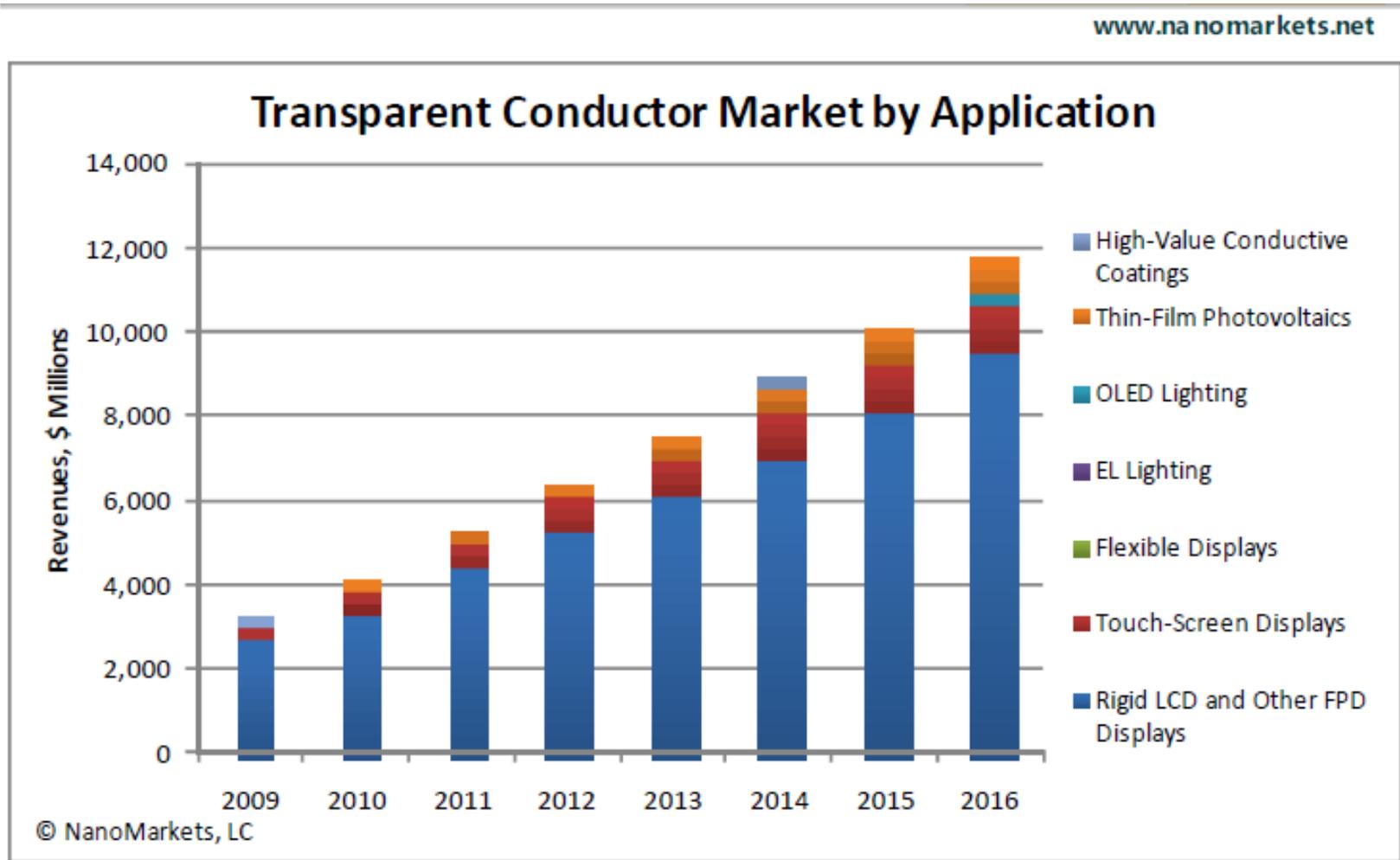
Transparent Electrodes: everywhere not where!

3



Transparent Electrodes: market forecast

4



Transparent Electrodes: materials and comparison

5

	ITO	AZO	CNT	Ag nanowire	Micro-nano-grid UTMF	Multilayer UTMF	AZO+ UTMF	Graphene
Transmission on glass (%)	80-90	80-90	60-90	80-90	65-80	60-75	80-90	70-95
Sheet resistance (Ohm/sq)	15-30	15-40	40-200	1-20	1-10	10-25	15-30	1-1000
Typical film thickness (nm)	100	200-800	<10	100	<5 + thicker grid	10-15	40-200	<5
Work function (eV)	4.8-5	4.5-4.85	4.9-5	4.3	4.3-5.3	4.3-5.3	4.3-5.3	4.5-4.6
Stability (damp heat, chemical, temperature)	****	**	*****	***	*****	*****	*****	*****
Max processing temperature (°C)	200	150-250	RT	100-200	RT	RT	150-250	>1000
Mechanical flexibility	*	*	*****	*****	*****	*****	****	*****
Uniformity	*****	*****	**	**	***	*****	*****	**
Material cost	>1000\$/kg for In	<10\$/kg	<200\$/kg	<200\$/kg	<35\$/kg	<35\$/kg	<35\$/kg	<200\$/kg

State-of-the-art (ITO)

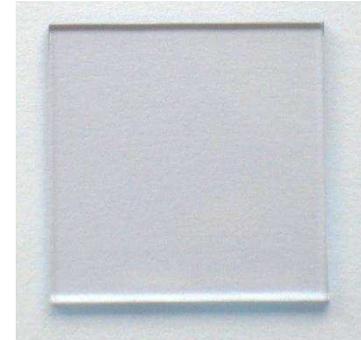
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Pros

- 50 years old material
- Excellent trade-off between electrical and optical properties

Cons

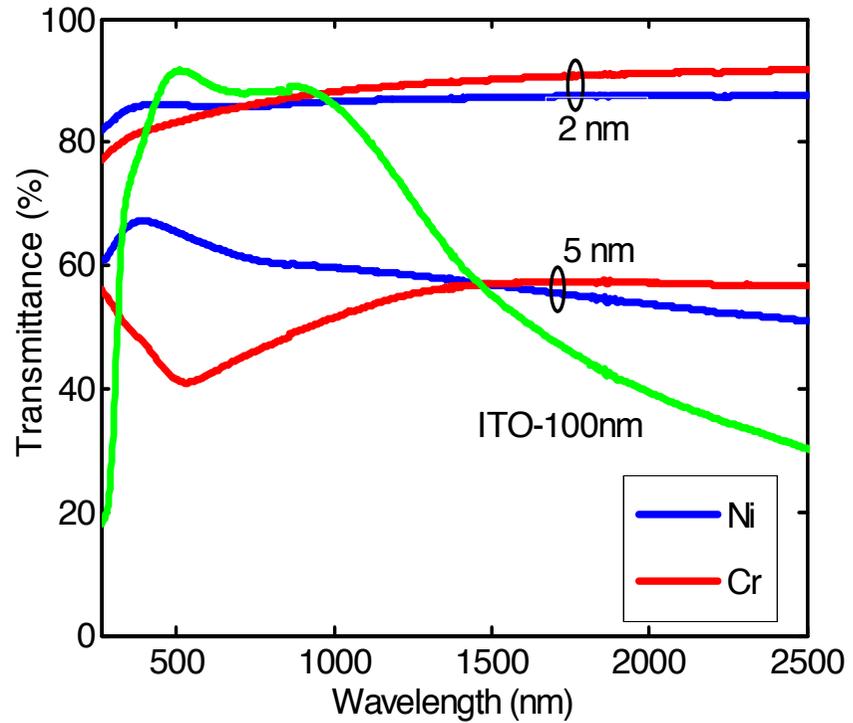
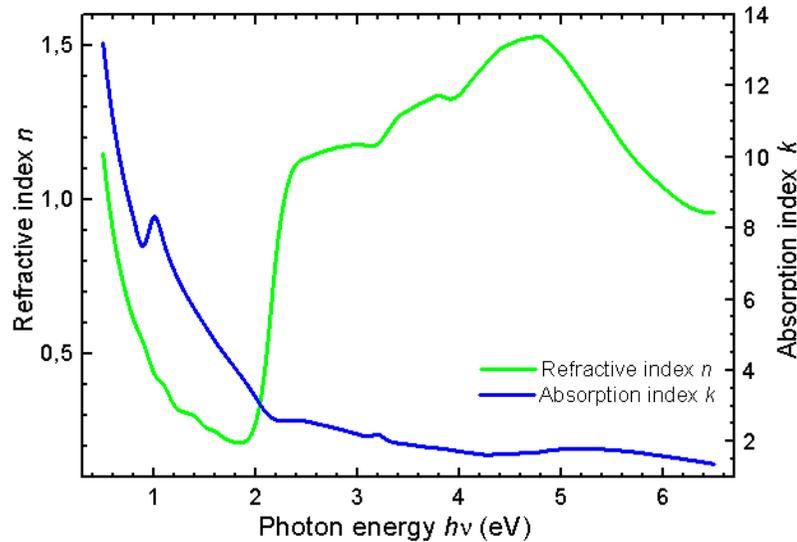
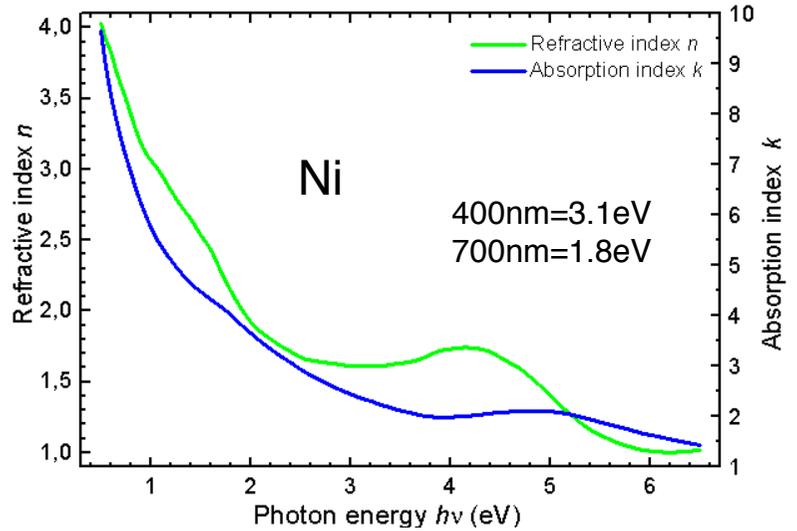
- Indium is scarce and expensive
- Incompatibility with other materials
- No mechanical-flexibility (essential for roll-to-roll)



Indium Tin Oxide (ITO)

Basics of UTMF: Optical properties

7



$$\omega_p = \sqrt{e^2 n_e / m \epsilon \epsilon_0}$$

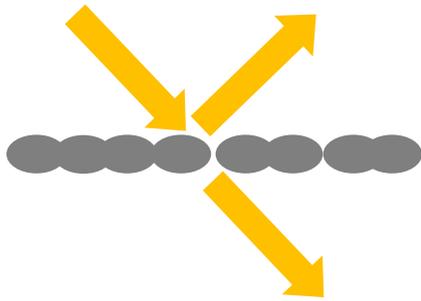
$$R = \left| \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \right|^2$$

$$\epsilon(\omega) = \underbrace{\epsilon - \epsilon \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2}}_{\epsilon'(\omega)} + i \underbrace{\frac{\epsilon}{\omega \tau} \cdot \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2}}_{\epsilon''(\omega)} =: (n + i\kappa)^2$$

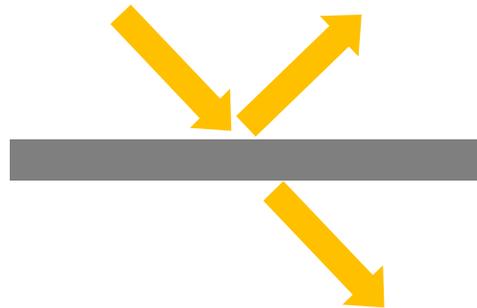
Sufficiently thin (<10nm) metal films can become transparent

Basics of UTMF: Optical properties

8



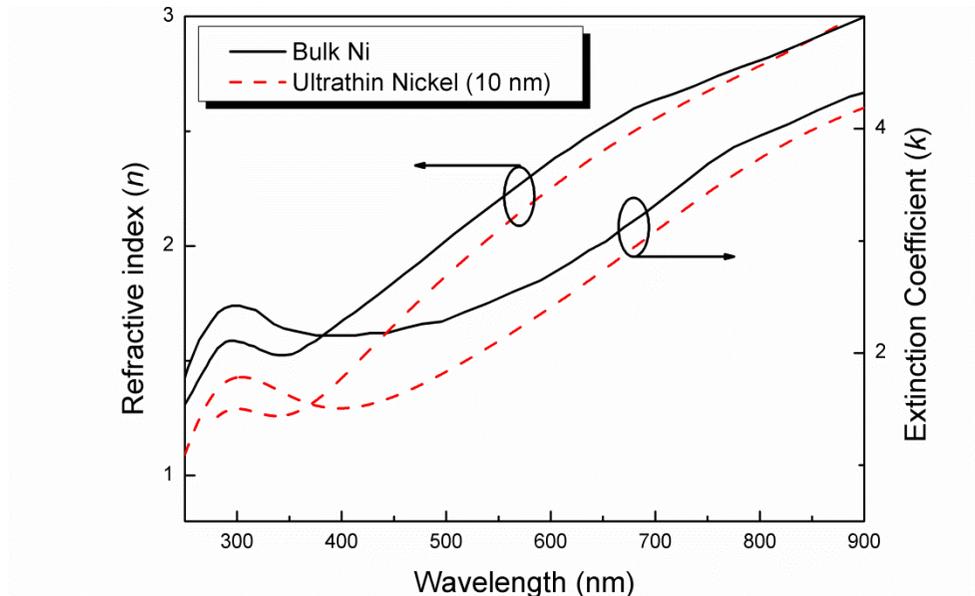
Metal islands



UTMFs-Semitransparent



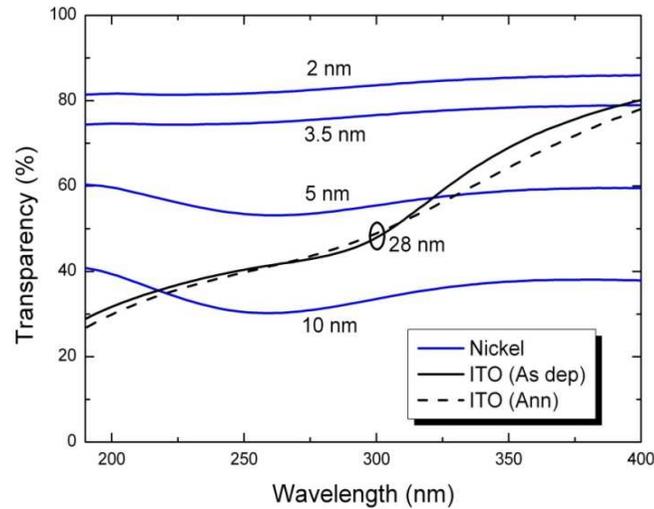
Thick film- Mirrors



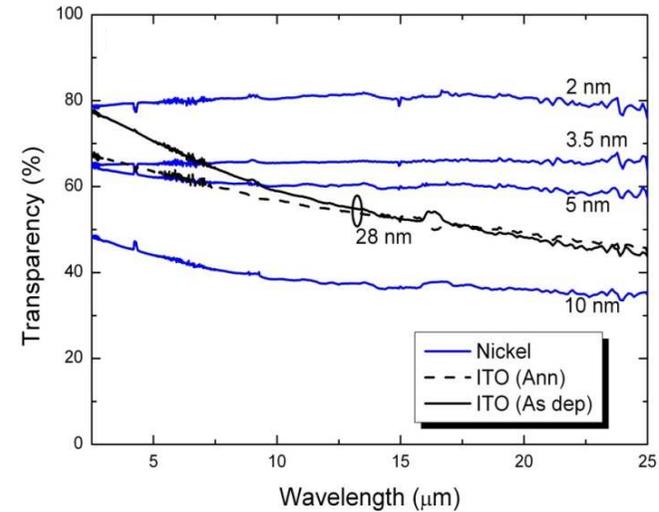
With reduction in thickness the optical constants change

UTMF vs. ITO in the UV → MIR

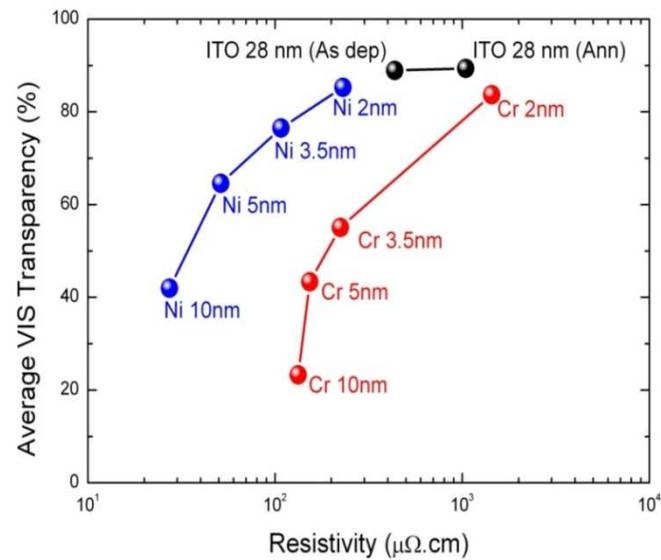
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UV



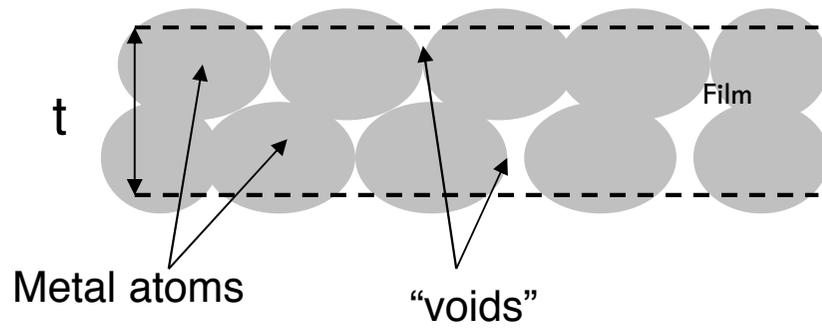
Mid-IR



Visible

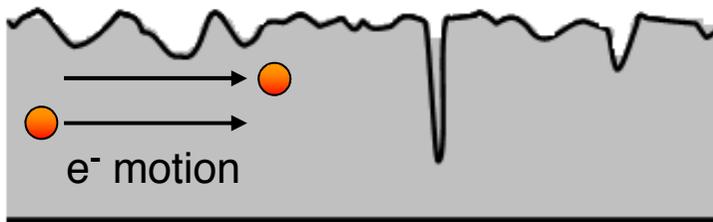
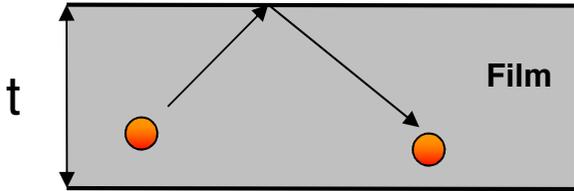
Basics of UTMF: Electrical properties

10



Defects + Phonons

Boundary scattering



Surface scattering

Basics of UTMF: Electrical properties

11

Fuchs-Sondheimer theoretical model

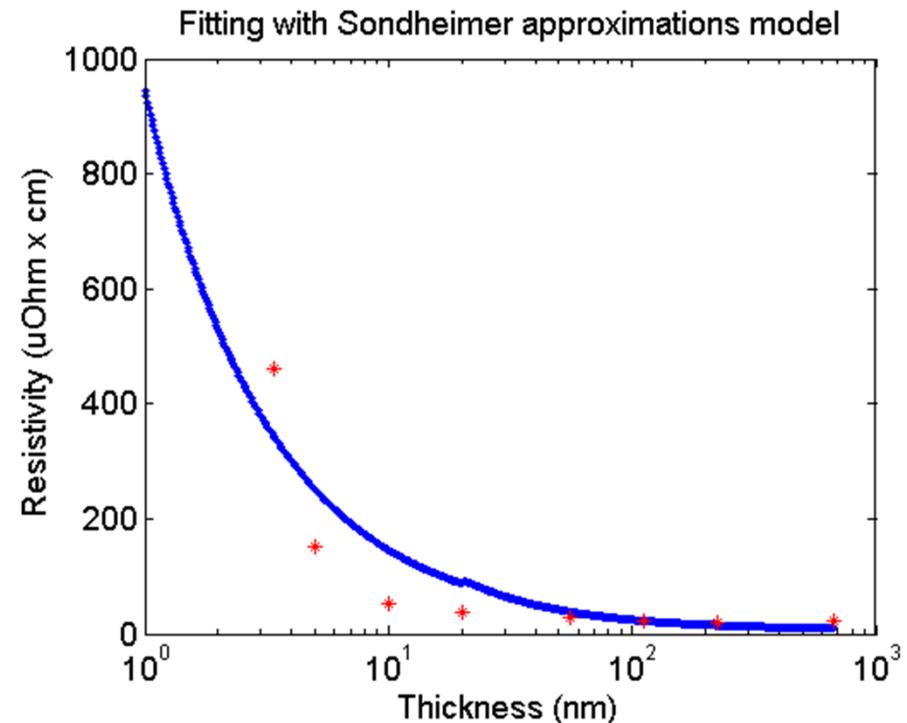
$$\frac{\sigma_{\infty}}{\sigma_{film}}(t) \approx \begin{cases} 1 + \frac{3}{8\kappa}(1-p) & \text{if } \kappa \gg 1 \\ \frac{4}{3} \frac{1-p}{1+p} \frac{1}{\kappa \log \frac{1}{\kappa}} & \text{if } \kappa \ll 1 \end{cases}$$

$$\kappa = t/l_{\infty}$$

t: film's thickness

l_{∞} : electron mean free path

p: specular parameter (=0 if diffusive, =1 if 100% specular)

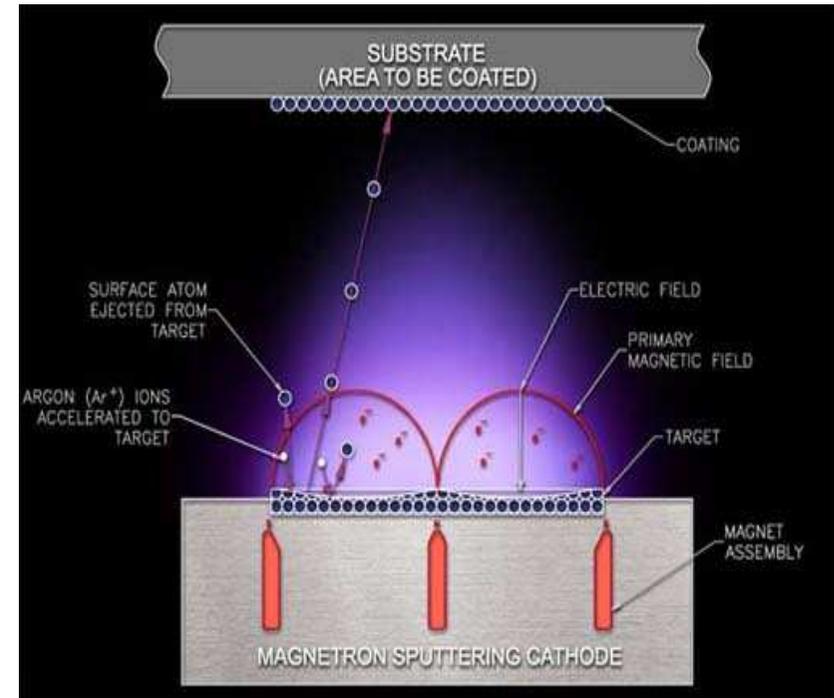


Bulk resistivity (Ω m): Ag=Cu= 1.65×10^{-8} , Ni= 7×10^{-8} , Ti= 4×10^{-7} , ITO= 2×10^{-6} , AZO= 5×10^{-6}

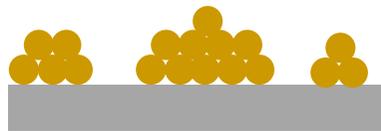
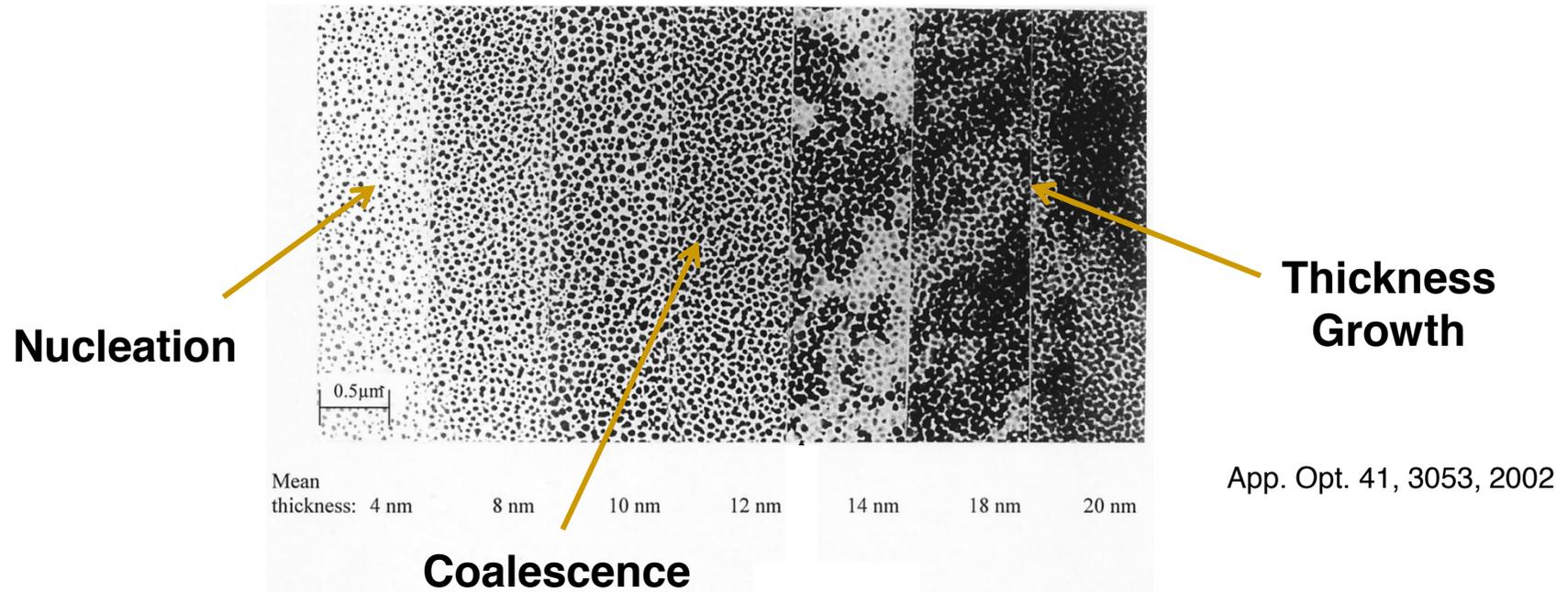
Deposition

12

- ❑ UTMFs are grown by **single step sputtering**
- ❑ The **substrate roughness** plays an important role
- ❑ Vacuum: $\sim 10^{-8}$ Torr
- ❑ Argon pressure: $1-8 \times 10^{-3}$ Torr
- ❑ Power: 20-100 DCW
- ❑ Dep. Rate: 0.3-1.5 Å/s
- ❑ Type of substrate used
 - ❑ **Glass**
 - ❑ **Silicon**
 - ❑ **LiNbO₃**
 - ❑ **PET**
 - ❑ **PEN**



UTMF growth mechanism



Island



Layer

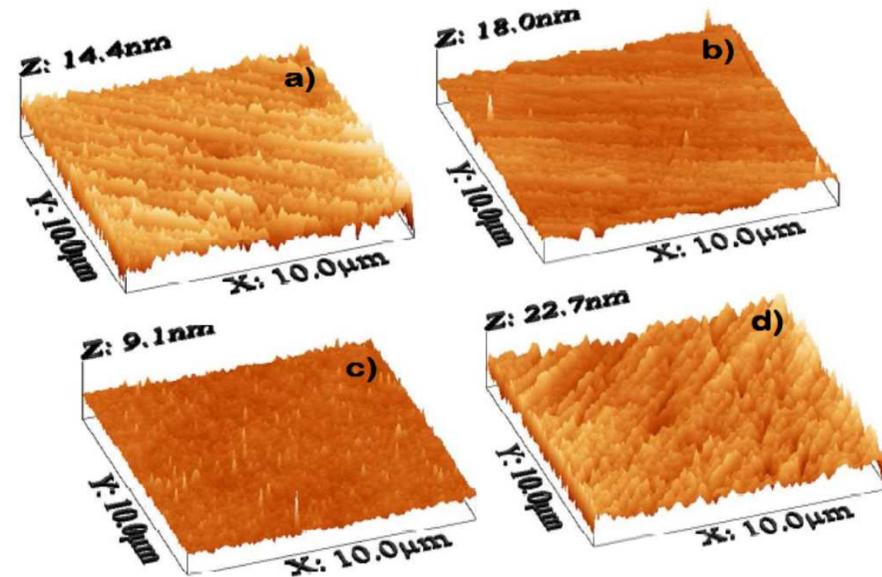


Mixed

AFM analysis

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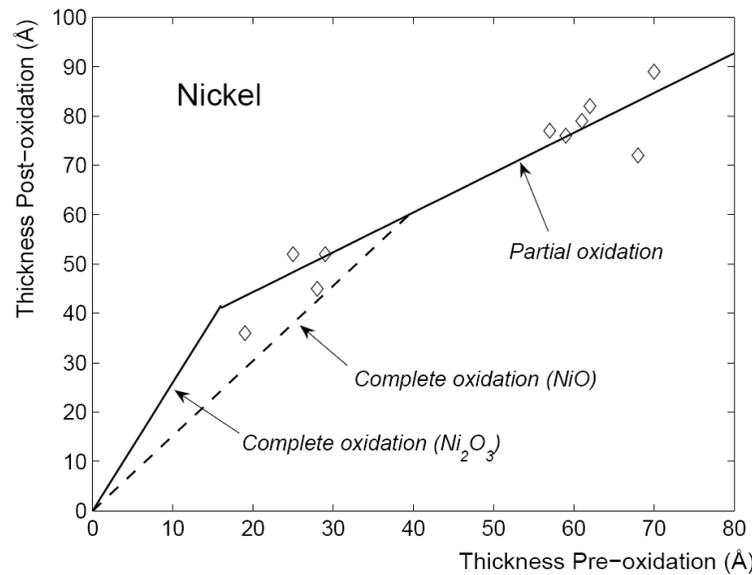
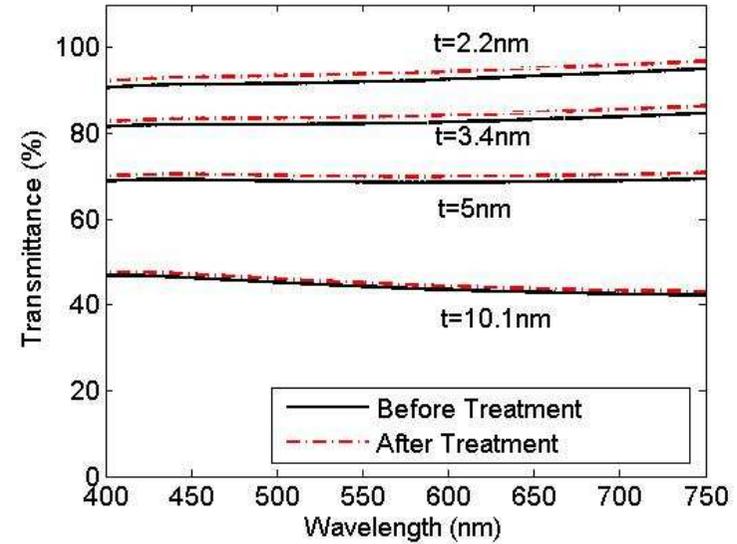
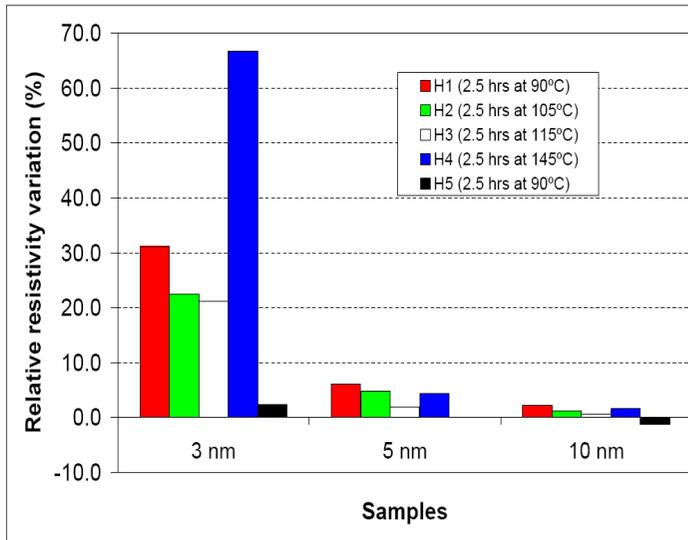
- ❑ Surface roughness is 1st indicator of films continuity
- ❑ Surface roughness must be kept below the layer's thickness
 - ❑ In our experiments, films roughness was found lower than 0.5 nm



a) ITO 100 nm, b) Ni 7 nm, c) Ni 9 nm,
b) and d) Ni 12 nm

UTMF passivation using surface oxidation

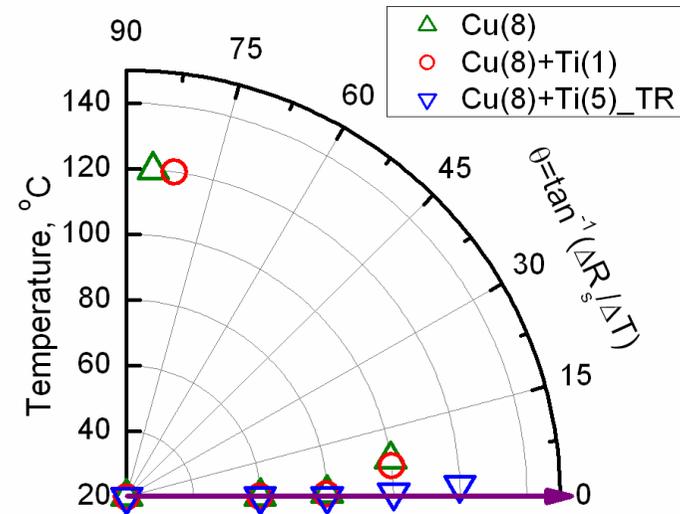
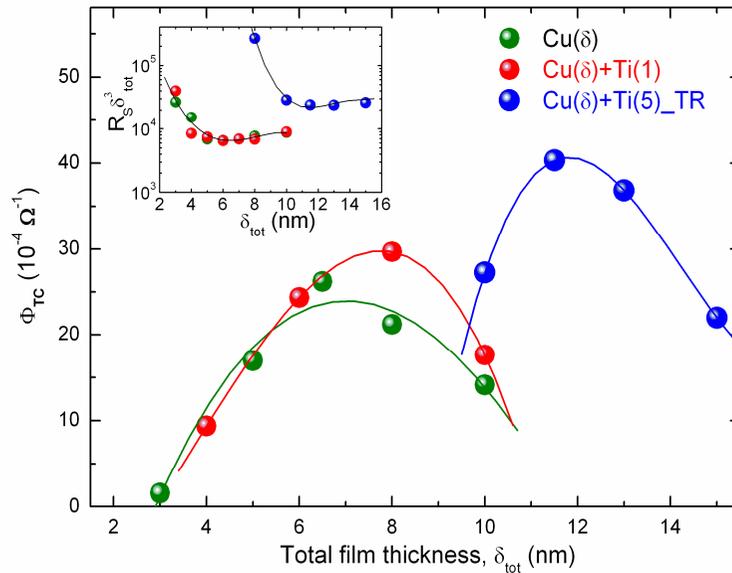
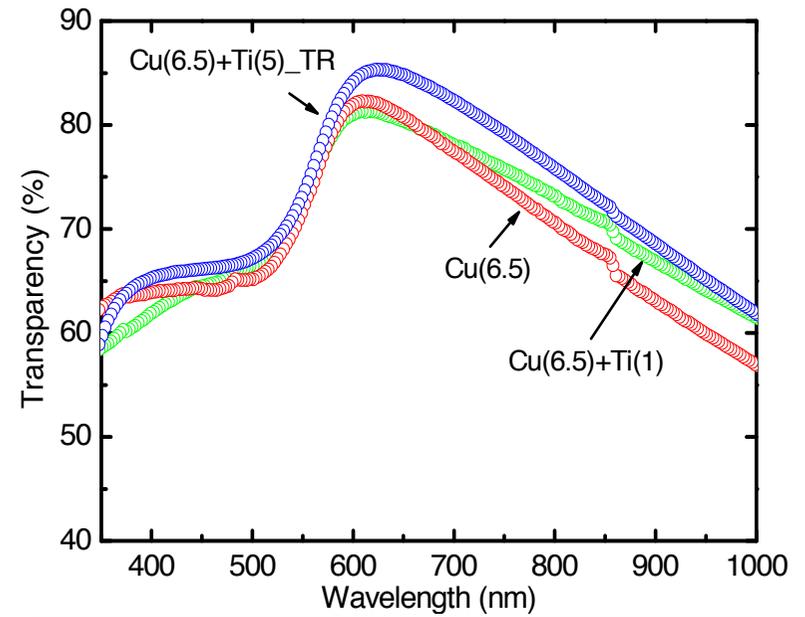
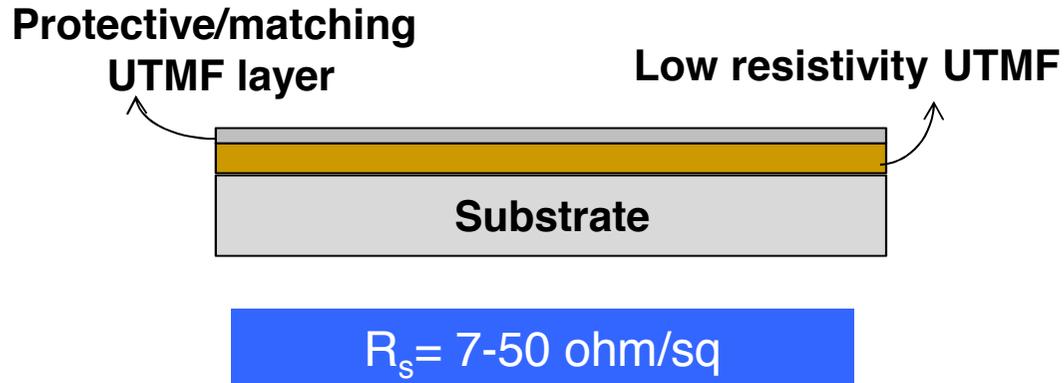
15



V. Pruneri, L. Martinez, S. Giurgola and P. Vergani, granted patent EP 213392

Multilayer UTMF (Cu+Ni)

16

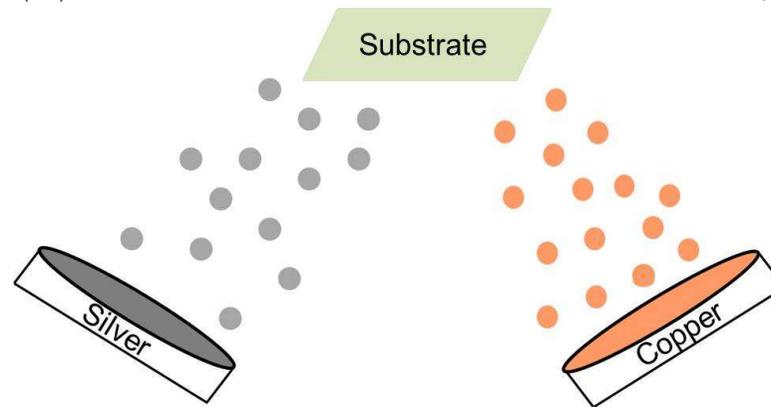
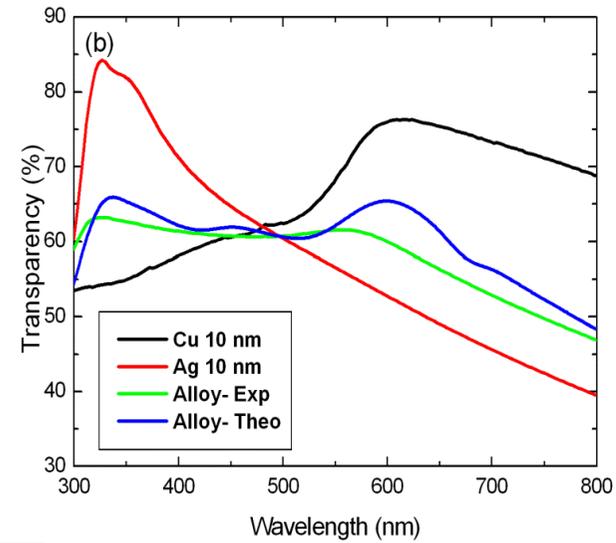
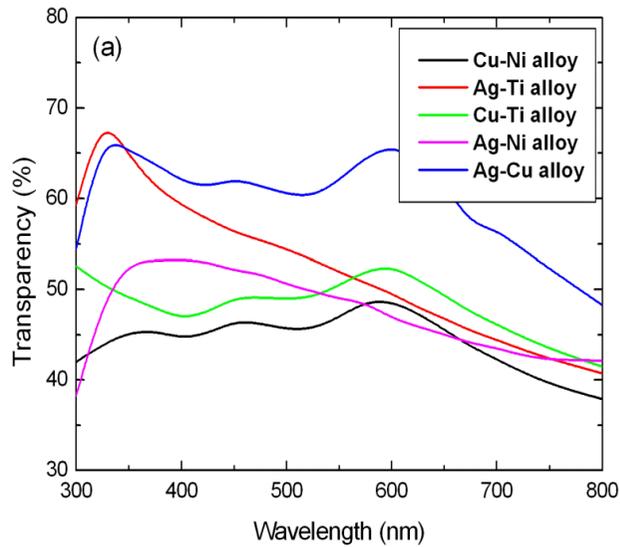


D. S. Ghosh et al., Appl. Phys. Lett. 96, 091106 (2010)

V. Pruneri, D.S. Ghosh and T.L. Chen, Patent application EP2317562 (2011) and WO2011054814 (2011)

Alloy UTMF (Ag/Cu- 50/50%)

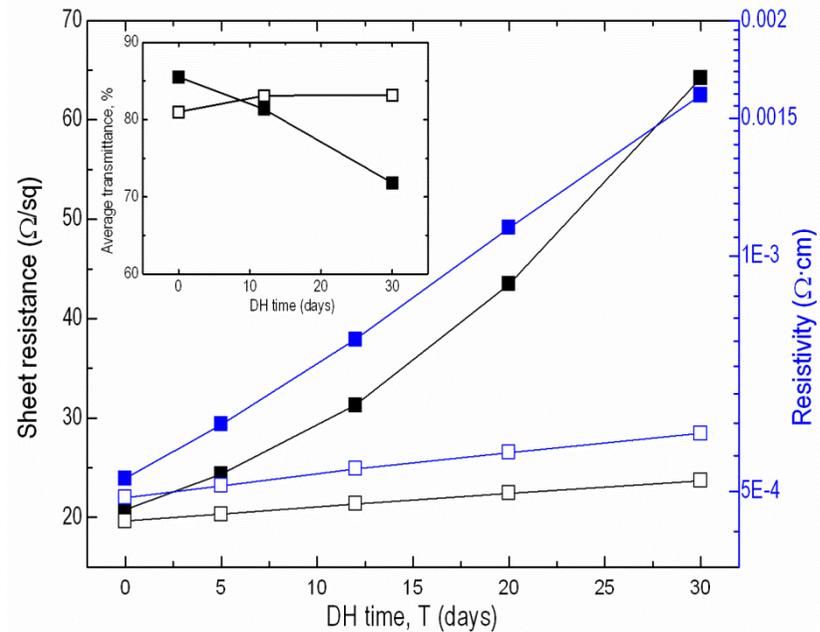
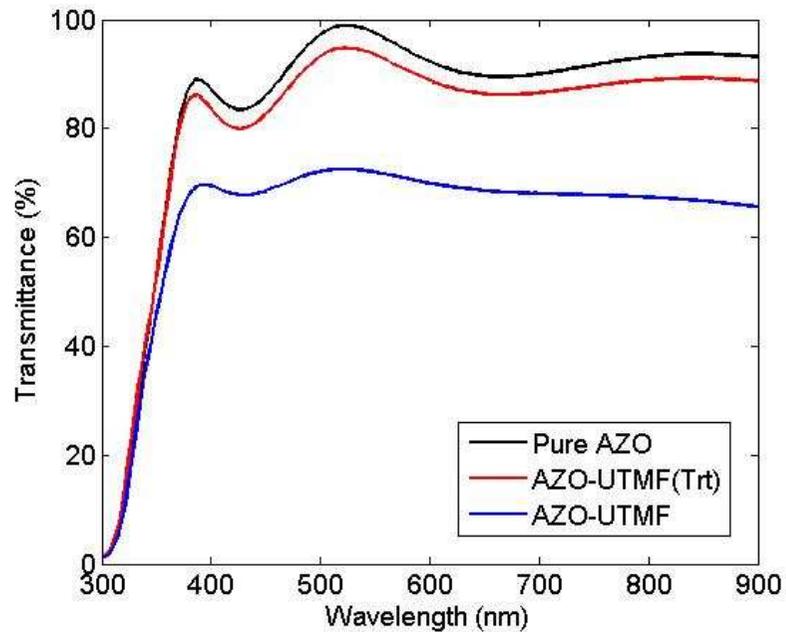
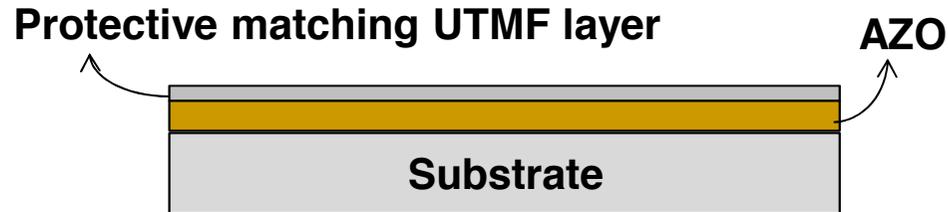
17



Flatter optical spectrum

Combining metals with AZO-I

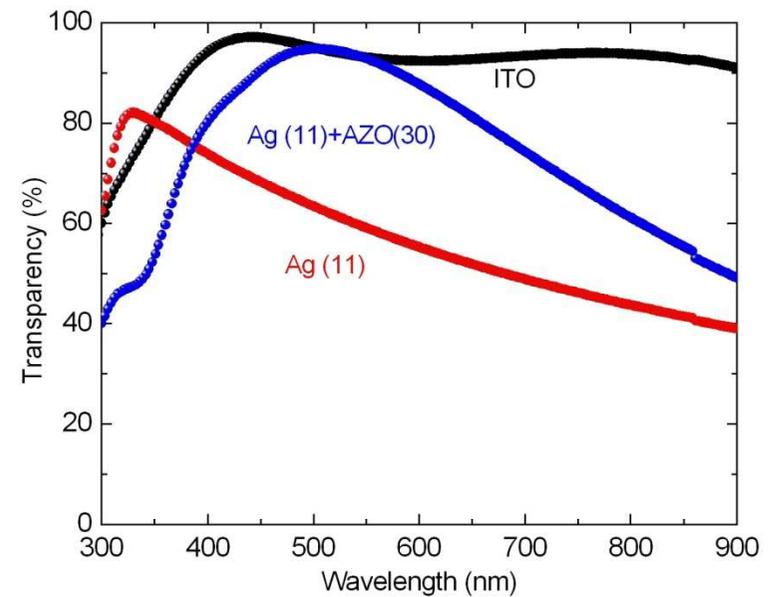
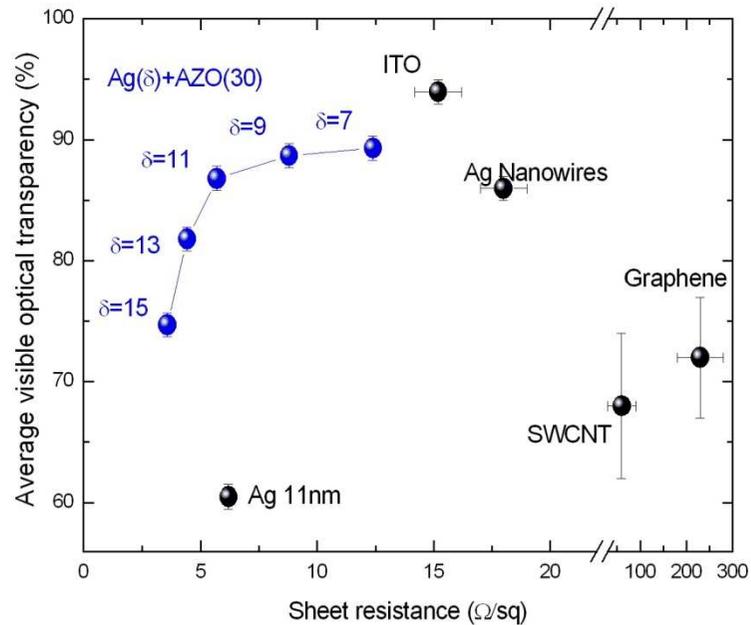
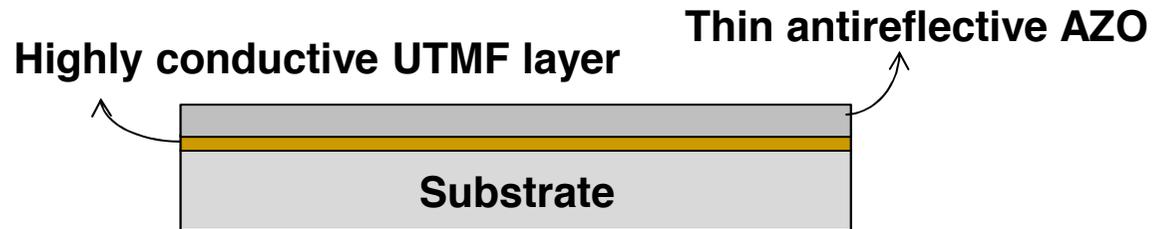
18



T. L. Chen et al., Appl. Phys. Lett. 99,93302 (2011); Appl. Phys. Lett. 100, 13310 (2012).
V. Pruneri, D.S. Ghosh and T.L. Chen, patent application ES 201030240 and WO101338 (2010)

Combining metals with AZO-II

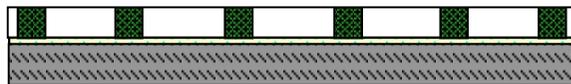
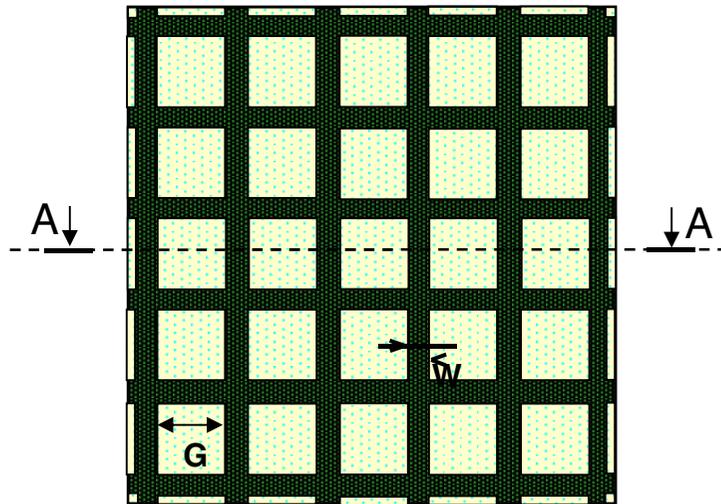
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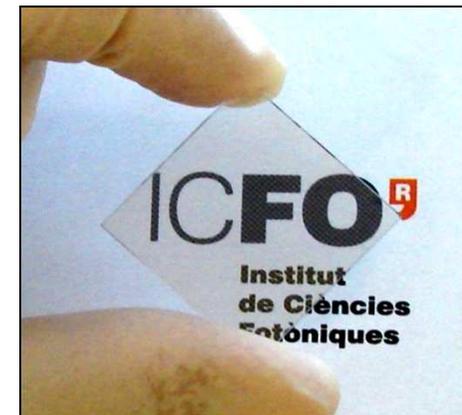
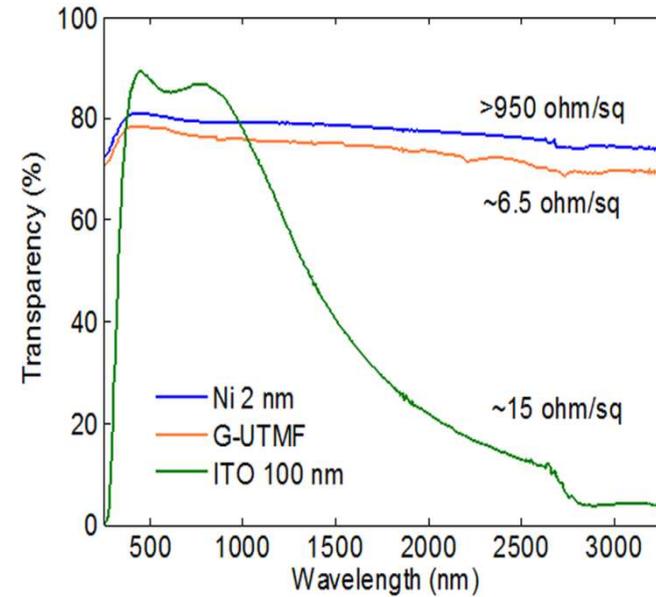
D. S. Ghosh et al., Appl. Phys. Lett. 96, 41109 (2010)

UTMF + micro-nano-grid

20



Significant reduction in sheet resistance

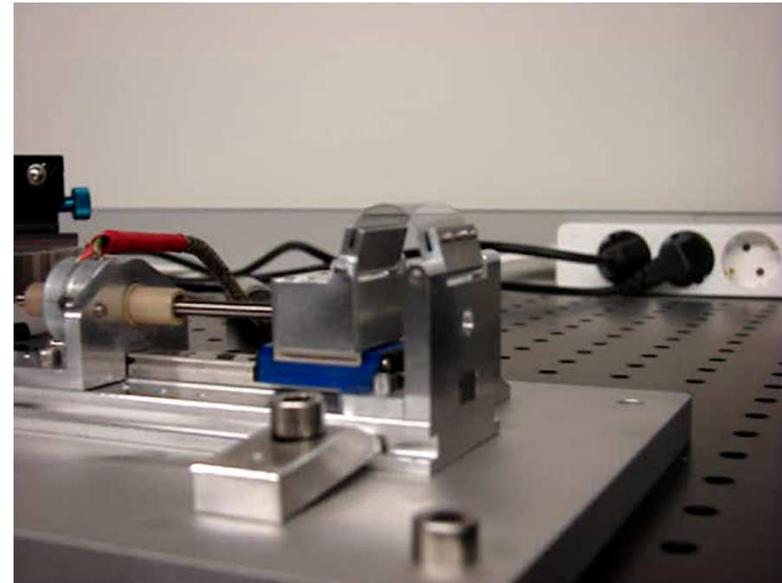
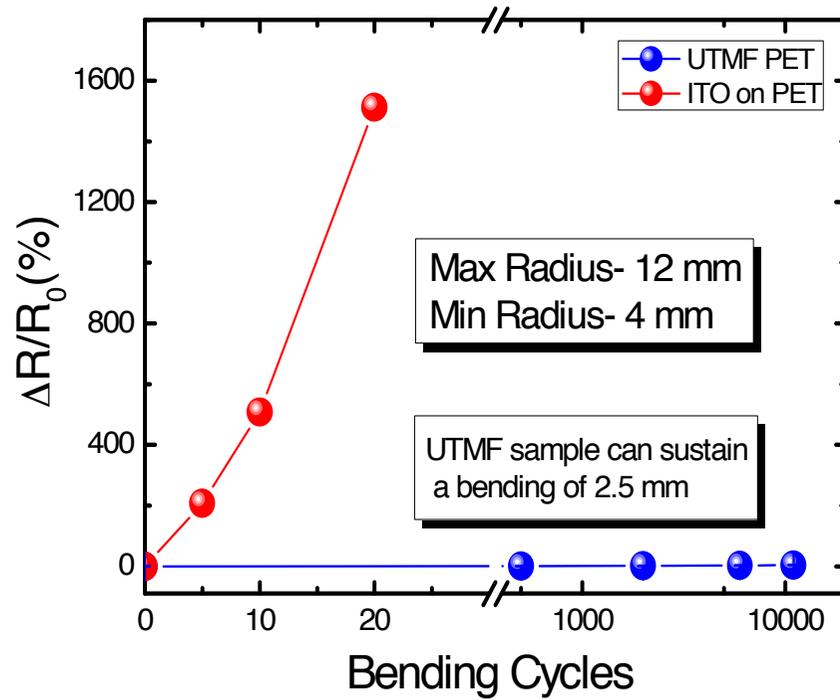


D. S. Ghosh et al., Appl. Phys. Lett. 96, 041109 (2010)

V. Pruneri and D.S. Ghosh, patent application EP 2259329 (2010) and WO2010136393 (2011)

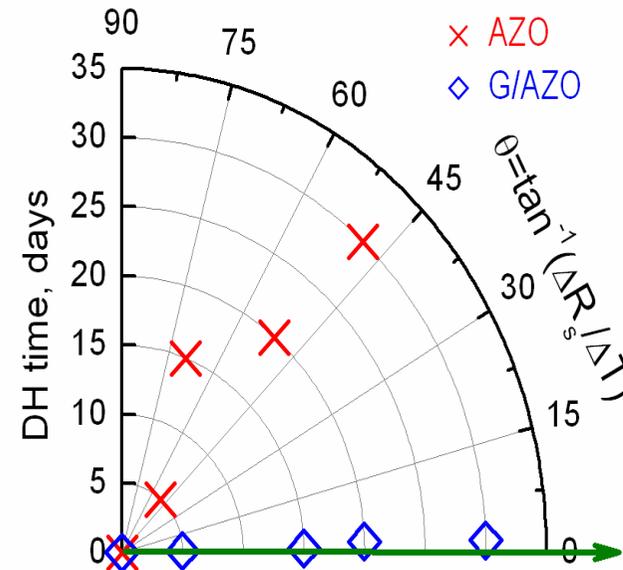
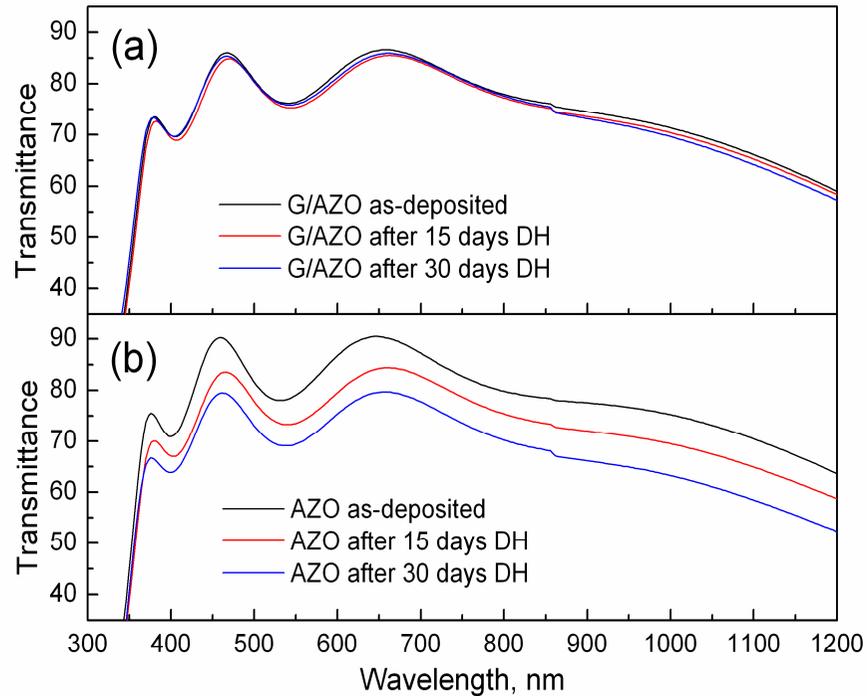
Mechanical Flexibility

21



Graphene as a anti-permeation layer

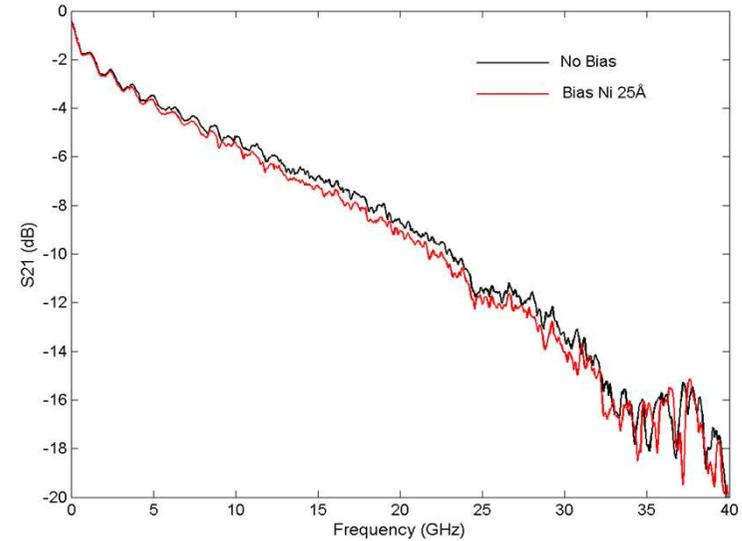
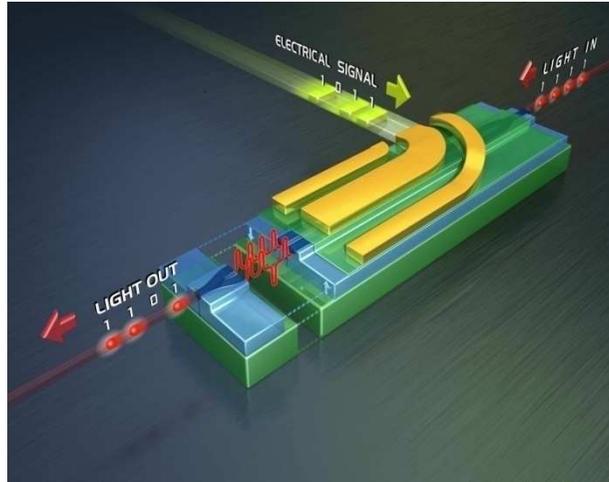
22



Graphene protects the underlying conducting layer in harsh environment

Application I: High speed electro-optic modulation

23

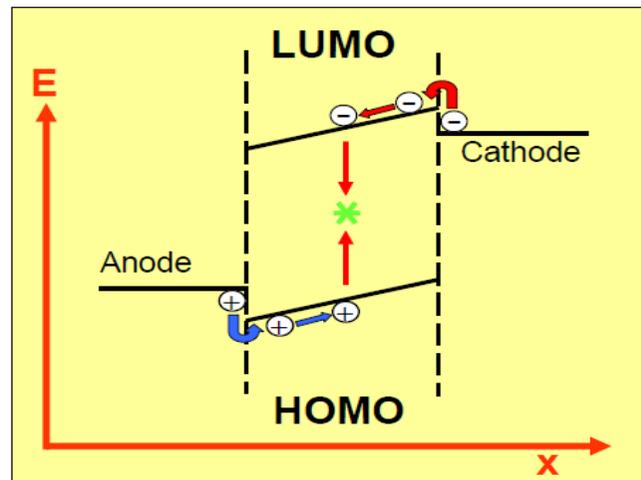
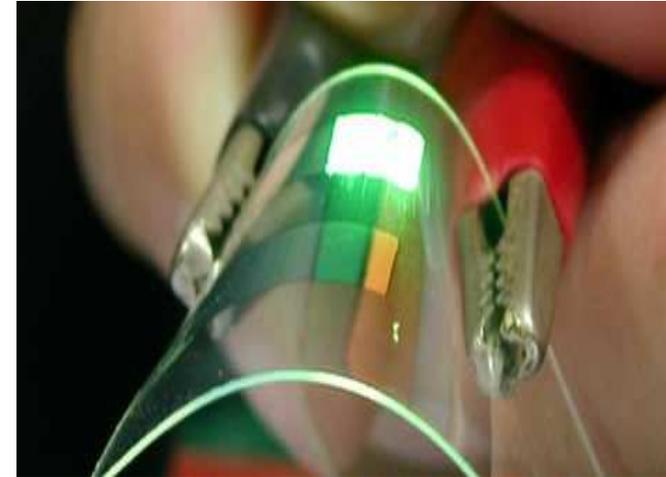
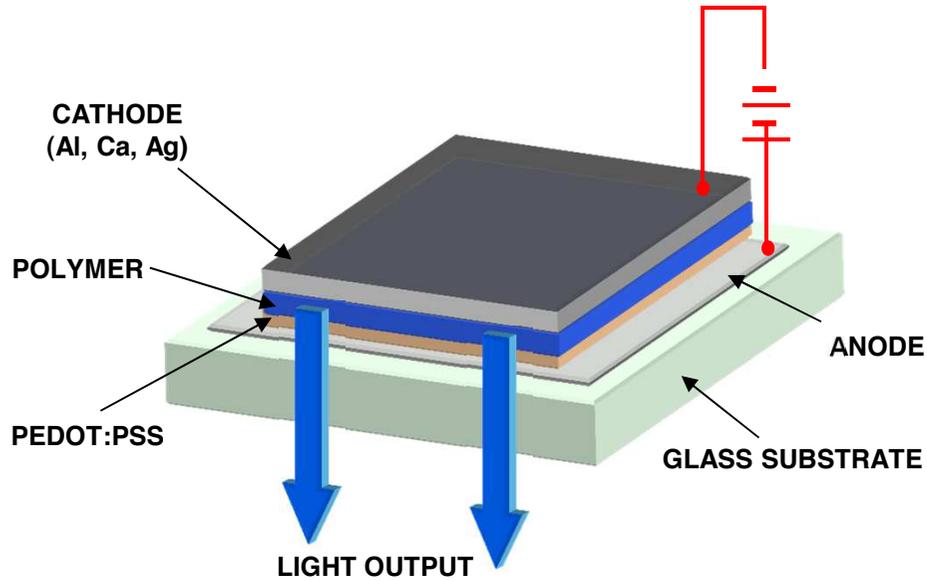


- ❖ New structure (US patent 11/070,931).
- ❖ Maximization of the electro-optic interaction length.
- ❖ Improvement of the modulator's linearity.
- ❖ Electro-optic response spectrum (S₂₁) for a modulator with an ultra thin metal bias electrode
- ❖ The presence of an ultra thin metal film does not affect significantly RF performances

M.Belmonte and V.Pruneri, granted patent US7127128

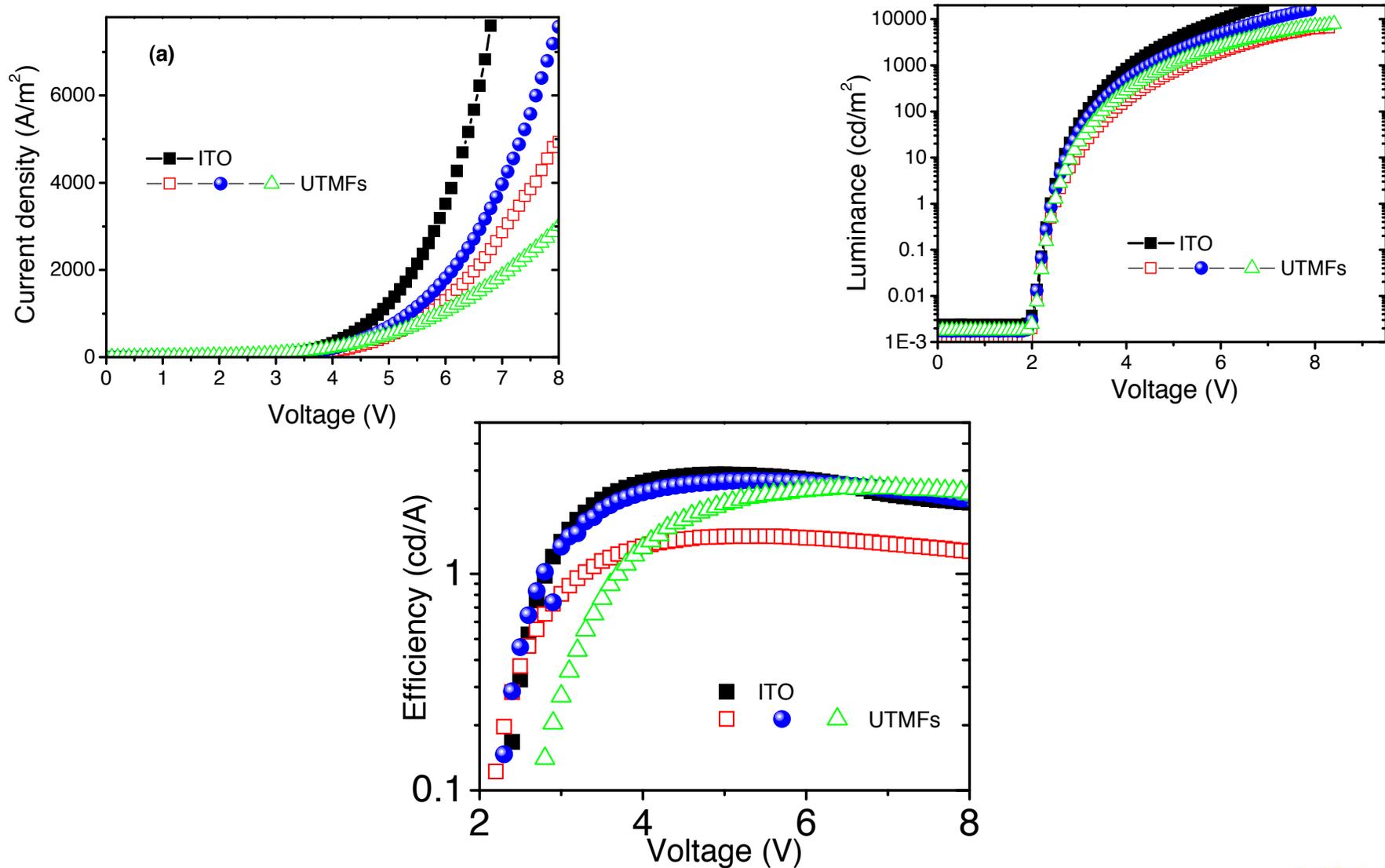
Application II: Organic Light Emitting Diode (OLED)

24



Application II: Organic Light Emitting Diode (OLED)

25

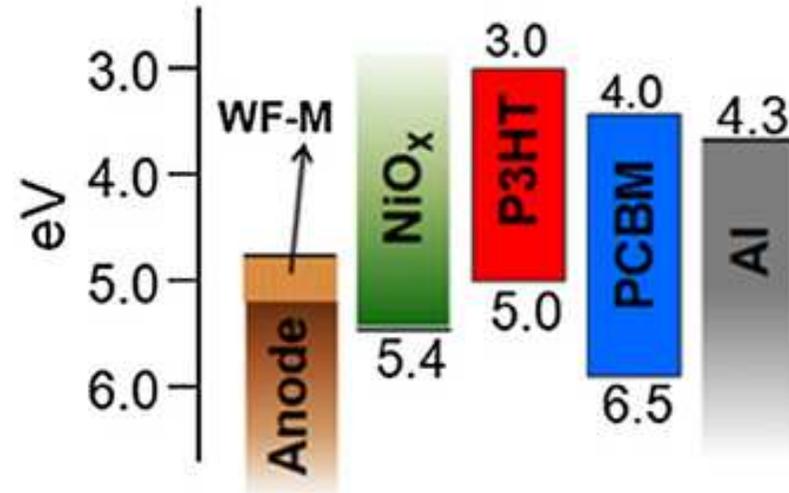
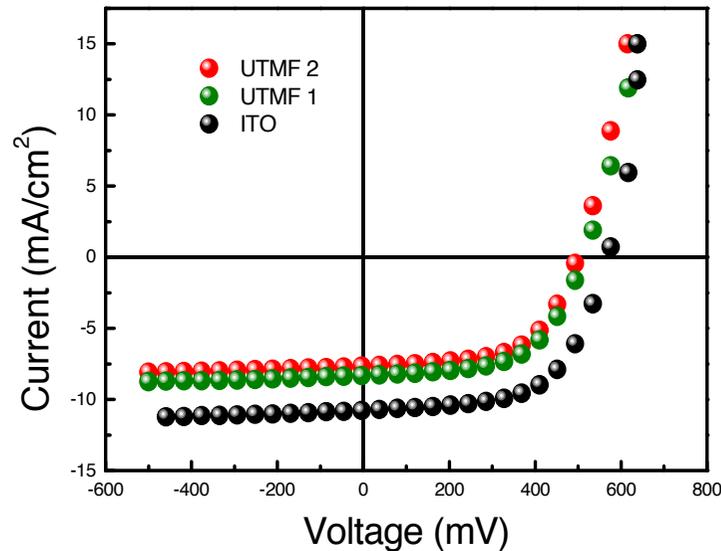
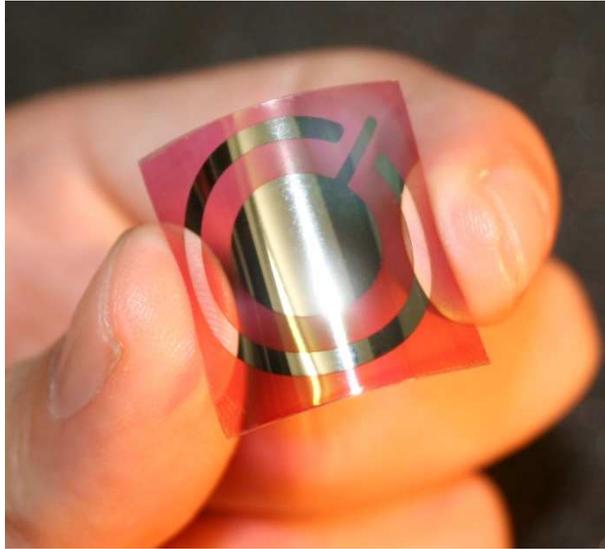


Similar performance with respect to state of art ITO

S. Cheylan et.al. Org. Elect. 12, 818, 2011; S. Cheylan et.al. Nanotec. 20, 275204(2009)

Application III: Organic Photovoltaics (OPV)

26

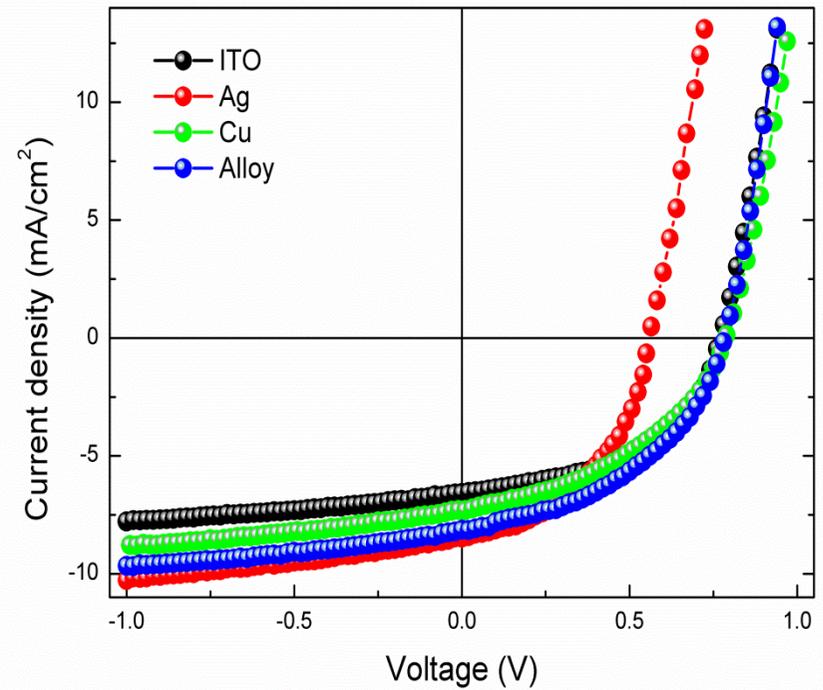
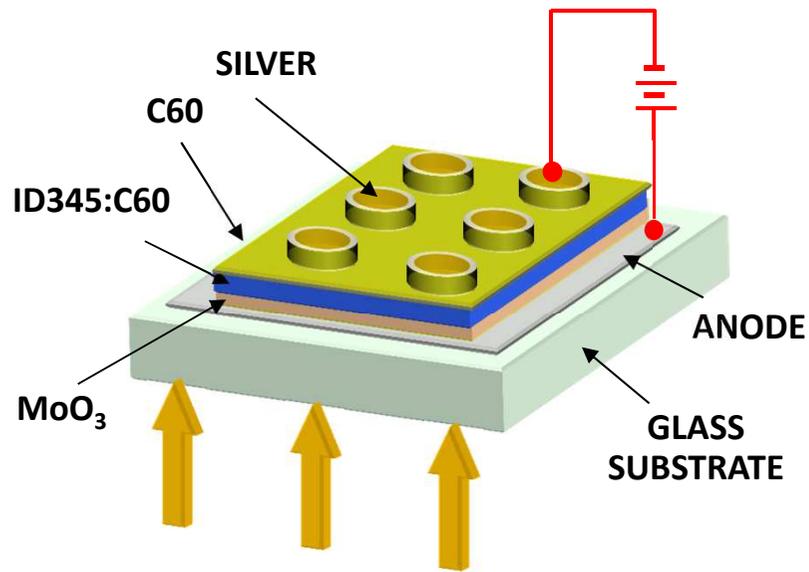


Recently we achieved the same efficiency as ITO

D. S. Ghosh et.al. Sol. Energ. Mat. Sol. C, 95, 1228 (2011), D. S. Ghosh et.al. Sol. Energ. Mat. Sol. C, 107, 338-343 (2012)

Application II: Organic Photovoltaics (OPV)-II

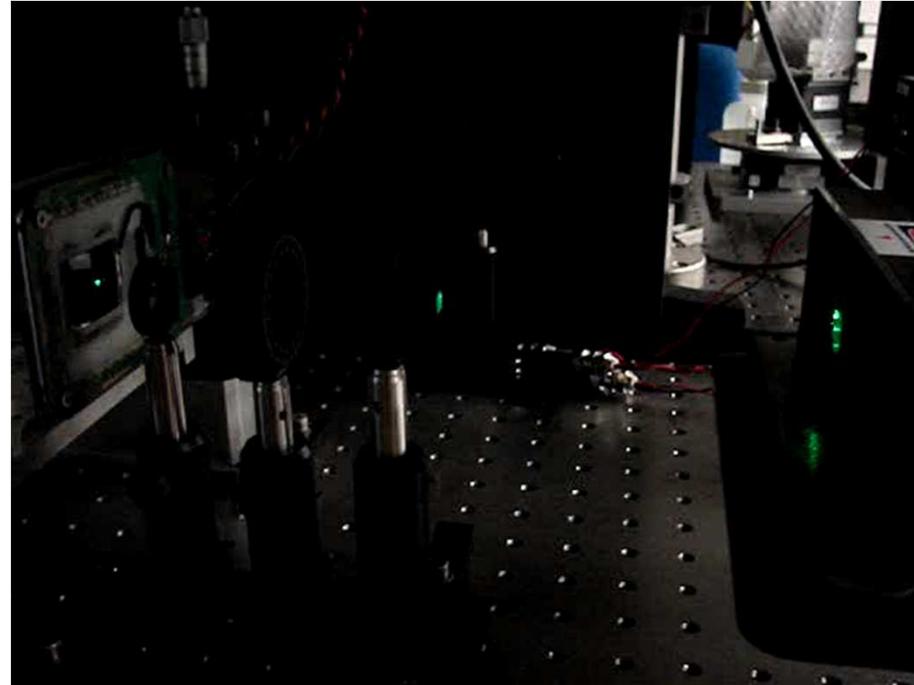
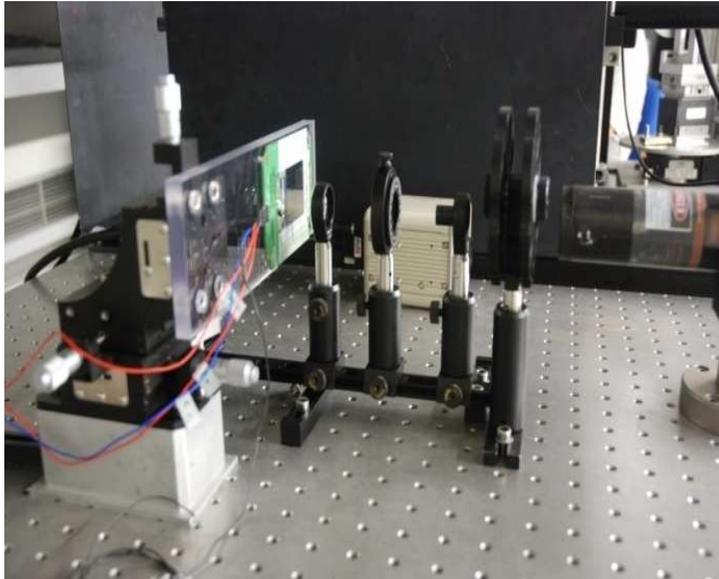
27



	R_s (Ω/sq)	WF (eV)	J_{sc} (mA/cm^2)	V_{oc} (mV)	ff (%)	η (%)
ITO	20	5.00	7.3	765	52	2.9
Cu	10	5.06	7.4	770	47	2.6
Ag	8	5.06	8.1	502	49	1.9
Alloy	15	5.06	8	770	47	2.9

Application IV: 3-D deflector cell

28



3-D cell LC requirements:

- ❖ $\pm 10^\circ$ deflection on horizontal axis
- ❖ 50 Hz frequency
- ❖ Integrability with LCD

Application V: Heads-up Display

29



UTMF



HUD requirements:

- ❖ Low cost for inexpensive cars
- ❖ Win solar light
- ❖ Reduce ghost image (double reflection from the windshield)
- ❖ Withstand vibrations and heat