Transparent electrodes: properties, applications and recent evolutions

Daniel BELLET
*Professeur Grenoble INP*
Laboratoire des Matériaux et du Génie Physique
daniel.bellet@grenoble-inp.fr

Jean-Pierre SIMONATO
*Directeur de Recherche CEA*
LITEN / DTNM
jean-pierre.simonato@cea.fr

*Midis Minatec, Grenoble, 25th May 2018*
Outline

- A short introduction
- Prevailing properties of Transparent electrodes (TE)
- Transparent conductive oxides (TCO)
- Carbon based TE
- Conductive polymers
- Metallic based (nano)materials
- Prospects and conclusive remarks
Transparent electrodes (TE): useful for what?

- Touch screen
- Transparent heaters
- Flexible LCD
- Flexible OLED
- Smart windows
- Medical applications (here thermotherapy)
- Flexible solar cells
- Electromagnetic applications (here flexible antennas)
Transparent electrodes: main features

- Transparent electrodes are in many devices for:
  - energy: solar cells, efficient lighting and smart windows
  - transparent heaters
  - displays
  - touch screens...

- All transparent electrodes are made from nanomaterials

- Efficient integration: search for specific properties and/or low cost and/or growth at low temperature...

- Expected properties: optical transparency, electrical conductivity, flexibility, haziness... without forgetting stability and environmentally friendly
# Transparent electrodes: TCO vs emerging TCMs

## Transparent Conductive Oxides (TCO):
- Indium Tin Oxydes (ITO)
- Fluor doped Tin Oxides (FTO)
- Aluminium doped Zinc Oxides (AZO)

**Advantages:**
- Well known and used
- Very good physical properties

**Drawbacks:**
- Brittle
- Can be scarce/expensive (In)
- Sometimes need of vacuum and/or high temperature

## Emerging TCMs:
- Graphene
- CNT
- Conductive polymers
- Metallic nanowire networks or grids

**Advantages:**
- Some appear to be promising
- New scientific area: exciting & place for imagination/innovation!
- Non fragile

**Drawbacks:**
- Not yet well known
- Stabilization?
- Could be expensive for some ...

Ellmer, Nat. Photonics, 6 (2012) 808
Klein, J. Am. Cer. Soc. 96 (2013) 331
Hecht et al., Adv. Mater. 23 (2011) 1482
Sannicolo et al., Small 12 (2016) 6052-6075
Outline

- A short introduction
- Prevailing properties of TE Transparent electrodes
- Transparent conductive oxides (TCO)
- Carbon based TE
- Conductive polymers
- Metallic based (nano)materials
- Prospects and conclusive remarks
Goal = fabricate and understand transparent electrodes:
  → good electrical conductor
  → good transparency in the visible (NIR).
  → Low cost (abundant materials and non toxic)

For some:
  → flexibility is crucial
  → low or high haziness (to be controlled)
  → can transport either electrons (n-type) or holes (p-type)

Applicative domains: photovoltaics, lighting, touch screens, electromagnetic applications, transparent heaters, sensors...
Properties of a good transparent electrode

Optimisation between electrical & optical properties → trade-off

- Flexible (if possible)
  (Flexible electronic market of about $40-50 billions in 2020)
Searched main properties of a TE (application dependent)

- Good electrical properties: \( R_{sh} \sim 10-100 \, \Omega_{/sq} \) or \( \rho < \text{few} \, 10^{-4} \, \Omega \cdot \text{cm} \)

- Good optical transparency: \( Tr \sim 85 - 90 \% \)

- Low cost (abundant materials and non toxic)

For some cases:
- Low or high haziness
- Flexibility (or even stretchability)
- Being able to transport electrons (n type) or holes (p-type)
Transparency versus electrical resistance: a trade-off

One figure of merit: $\text{FoM} = T^{10}/R_{sh}$

Sannicolo et al. Small 12 (2016) 6052
Outline

- A short introduction
- Prevailing properties of TE Transparent electrodes
- Transparent conductive oxides (TCO)
- Carbon based TE
- Conductive polymers
- Metallic based (nano)materials
- Prospects and conclusive remarks
Transparent Conductive Oxides (1)

TCO = thin oxide layer (t≈ 200-300 nm)
Main requirements:

- high electrical conductivity ($\sigma$)
- low optical absorption ($\alpha$):

$\sigma / \alpha$ should be as large as possible

$\sigma = \frac{1}{\rho} = n_c \mu(n_c) e$

$R_{sh} = \rho = \frac{1}{t \ n_c \mu e t}$

**Transparent Conductive Oxides (2)**

**Electrical conductivity:**

\[ R_{sh} \downarrow \iff n_c \uparrow ; \mu \uparrow ; t \uparrow \]

\[ R_m \omega \mu = f(n_c) \]

**Optical transmittance:**

*absorption* \(\downarrow\) \(\iff\) *\(n_c\) and \(t\) \(\downarrow\)*

---

*I. Hamberg et al., J. Applied Physics (1986)*

*G. Rey, Thesis Grenoble (2012)*
Conductivity of films depends on different electrons scattering mechanisms:

- Scattering probability:

\[ \frac{dP(t)}{dt} = \frac{dP(t)}{\tau_1} + \frac{dP(t)}{\tau_2} + \frac{dP(t)}{\tau_3} = \frac{dP(t)}{\tau_{tot}} \Rightarrow \frac{1}{\tau_{Total}} = \sum_i \frac{1}{\tau_i} \]

- Conductivity:

\[ \sigma = -n_e e \mu_e = \frac{n_e e^2 \tau}{m} = \frac{1}{\rho} \]

\[ \Rightarrow \rho_{Total} = \frac{1}{\tau} \]

- Matthiessen law:

\[ \rho_{Total} = \sum_i \rho_i = \rho_{bulk} + \rho_{GB} + \rho_{GB} + \rho_{surf} \]
Transparent conductive Oxides: varying the haziness (4)

Control of light scattering is important

Transmission totale: directe + diffuse

T. Chih-Hung et al., Organic Electr. 12 (2011) 2003

Giusti et al., ACS Appl. Mat. & Interf. 6 (2014) 14096
Outline

- A short introduction
- Prevailing properties of TE Transparent electrodes
- Transparent conductive oxides (TCO)
- Carbon based TE
- Conductive polymers
- Metallic based (nano)materials
- Prospects and conclusive remarks
Carbon based Transparent electrodes

The percolation concept

*Percolare*
"to filter" or "trickle through"

**De et al., ACS Nano 4 (2010) 7064-7072**
**Langley et al., Nanotechnology 24 (2013) 452001**
**Sannicolo et al., Nano Letters 16 (2016) 7046**
Carbon based Transparent electrodes

- Carbon Nanotubes
- Graphene

Typical sheet resistance ~ few hundreds/kilos ohm.sq$^{-1}$ @ 90%

Difficult scale-up (defects and grain boundaries, cost)

Bae et al. Nature Nanotechnology, 2010
Outline

- A short introduction
- Prevailing properties of TE Transparent electrodes
- Transparent conductive oxides (TCO)
- Carbon based TE
- Conductive polymers
- Metallic based (nano)materials
- Prospects and conclusive remarks
Conductive Polymers – Ultraconductive materials

PEDOT:PSS
σ = 0.1 S.cm⁻¹
Big counter-ions
Excess counter-ions
Non treated

PEDOT:OTf
σ = 1218 S.cm⁻¹
Small counter-ions

PEDOT:OTf-NMP
σ = 3630 S.cm⁻¹
Slower polymerization rate

PEDOT:Sulf-NMP
σ = 5462 S.cm⁻¹
Triflate substitution
Oxidation level ↑

- Increase of structural order
- Increase of grain size
- Increase of oxidation level (acid treatment)
- Increase conduction in amorphous PEDOT
- Metallic behaviour + optimized disorder

Gueye et al., Chem. Science 6 (2015) 412
Gueye et al., Chem. Mater. 28 (2016) 3462
Conductive Polymers – First demo for film heaters

57 Ω sq⁻¹ @ 88 %
Haze < 1 %
Up to 10 000 W m⁻²

Patent pending to CEA
Conductive Polymers – First demo for film heaters

Des films polymères à la fois chauffants et transparents

Le Liten, institut de CEA Tech, vient de breveter le tout premier film chauffant transparent 100% polymère. Ce dernier pourrait remplacer avantageusement les matériaux existants dans des applications d'électrodes et de films chauffants transparents. […]
Outline

- A short introduction
- Prevailing properties of TE Transparent electrodes
- Transparent conductive oxides (TCO)
- Carbon based TE
- Conductive polymers
- Metallic based (nano)materials
- Prospects and conclusive remarks
Metallic based transparent electrodes: metallic grids

Metals are conductive but absorb too much light

→ one can play with spatial distribution or thickness

→ metallic grids or nanowire networks (percolation)

Metallic grids

Metallic nanowire networks
Metallic based transparent electrodes: silver nanowire networks

AgNO₃
Metallic based transparent electrodes: silver nanowire networks
Resistance measured during thermal ramp

Mechanisms involved:
➢ desorption
➢ sintering
➢ instabilities

Langley et al., Nanoscale 6 (2014) 13535
How do AgNW networks perform?

For sheet resistance of about 10 Ω/sq:

Sannicolo et al. Small 12 (2016) 6052
Stability of AgNW networks under electrical stress

- In-situ observation of crack occurrence and propagation during electrical stress

*T. Sannicolo et al., ACS Nano 12 (2018) 4648-4659*
A way to enhance AgNW networks stability: SALD

- Very conformal coating of AgNWs by ZnO or Al₂O₃ by atmospheric pressure ALD


- Similar conclusions for CuNW networks

C. Celle et al., Nanotechnology 29 (2018) 085701
Outline

A short introduction

Prevailing properties of TE Transparent electrodes

Transparent conductive oxides (TCO)

Carbon based TE

Conductive polymers

Metallic based (nano)materials

Prospects and conclusive remarks
Prospects and conclusive remarks

Still a lot of work to be done on TCM

*Ex.: p-type TCOs, better controlled of properties (WF, haze, flexibility...), processes at lower temperature, nature & properties of interfaces...*

Some serious alternatives: conductive polymers, metallic nanowire networks...

Stability must be considered *(chemical, thermal, ageing, electrical...)*

A lot of studies and innovations facing us: architectures, multilayers, hybrids...

Various applications

*Not just one TCM will win!* The choice will depend on applications specificities
Prospects and conclusive remarks
Prospects and conclusive remarks

“safer by design approach”
Thank you!

to all our students & colleagues

to our funders

and to you for your attention!