Graphene: potential ITO - replacement as transparent conductive layer

Maria Losurdo and Giovanni Bruno
National Council of Research
Institute of Inorganic Methodologies and of Plasmas, Bari, Italy
maria.losurdo@cnr.it
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The Modular MEM4WIN Window Concept

ADVANCED TECHNOLOGIES FOR SMART WINDOWS

Modular components like
• OPVs
• organic light emitting diodes (OLEDs)
• micro mirrors
• solar thermal collector
will be integrated into a quadruple glazing window

As innovation, in the OPV and OLED, GRAPHENE will replace ITO
Motivation: Getting Graphene into the ITO Replacement market

Materials combining high electrical conductivity and optical transparency are vital for optoelectronic devices, such as solar cells, light emitting diodes and touch screens.

Doped metal oxides, in particular indium tin oxide (ITO), are the most widely used.

However, the rising price and limited geographical availability of Indium and the desire for flexible substrates necessitates alternative transparent conductor materials (TCs) for next generation devices.

There are a number of technologies being developed to address this market, many of which are based on some form of nanomaterials and involve printing or coating processes which can be performed continuously.

Among the range of intensely studied emerging TCs, graphene shows great promise.

Comparison of the various nanomaterials competing in the ITO replacement space. [Source: Touch Display Research]
Graphene: Revolution in Waiting

- From Graphite to Graphene: a single layer of Carbon atoms in a honeycomb structure 3.4 Å thick

Graphene is the thinnest material ever made; it is transparent, conducts electricity and heat better than any copper wire and weighs next to nothing. Its thinness makes the material ultra-flexible, even rollable.
Why Graphene is so Popular?-1

Its history leading to the Nobel Prize in Physics in 2004

- The term graphene first appeared in 1987 to describe single sheets of graphite.
- In the 1930s, Landau and Peierls showed thermodynamics prevented 2D crystals in free state, an article in Physics Today reads:

  "Fundamental forces place insurmountable barriers in the way of creating 2D crystals...Nascent 2D crystallites try to minimize their surface energy and inevitably morph into 3D structures. But there is a way around the problem. Interactions with 3D structures stabilize 2D crystals. So one can make 2D crystals sandwiched between or placed on top of the atomic planes of bulk crystals”

- In 2004, Andre Geim and Kostya Novoselov at Manchester University managed to extract single-atom thick crystallites (graphene) by the Scotch tape technique from bulk graphite and transferred them onto SiO₂ on a Si wafer.

- Since 2004, an explosion in the investigation of graphene in terms of synthesis, properties and applications have been reported.
## Why Graphene is so Popular?

### Its Outstanding (theoretical) Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Graphene</th>
<th>Competitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Electron Mobility (cm²/Vs)</td>
<td>200,000</td>
<td>Silicon 1400</td>
</tr>
<tr>
<td>High Electrical Conductivity (S/m)</td>
<td>$10^8$</td>
<td>Silver $63 \times 10^6$</td>
</tr>
<tr>
<td>Optical Properties</td>
<td>97.7% Transmittance (monolayer)</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity (W/mK)</td>
<td>5300</td>
<td>Silver 429</td>
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<tr>
<td></td>
<td></td>
<td>Copper 400</td>
</tr>
<tr>
<td>Mechanical Properties</td>
<td>High Young’s modulus 1100 Gpa</td>
<td>200 times stronger than steel</td>
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<tr>
<td></td>
<td>High Fracture Strength 125 GPa</td>
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<tr>
<td>Anomalous quantum Hall effect</td>
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</table>

### How it appears

- SEM microscopy image of graphene on glass
- Photograph of graphene on glass
Why Graphene as ITO-Replacement?

Focusing on Transmittance and Sheet Resistance

- 1-4 layers of graphene have comparable or even higher transmittance than ITO.
- In terms of sheet resistance, 4 layers of graphene (sheet resistance $\sim 30 \ \Omega/\square$) should be roughly equivalent to ITO on glass (sheet resistance $\sim 20–30 \ \Omega/\square$).

Integral transmittance of light ($\lambda = 350–800 \ \text{nm}$) illuminating 1.1-mm-thick glass and graphene (ITO) as a function of number of graphene layers and ITO thickness.

- Experimentally, it is challenging to achieve a sheet resistance $< 100 \ \Omega/$sq with optical transmittance $> 90%$
- Sheet resistance also strongly depends on graphene synthesis.
Synthetic Routes to Graphene

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Mechanical Exfoliation of Graphite

- Also known as the "Scotch™ tape" method
- Individual layers are peeled off of Kish graphite and deposited on an arbitrary substrate with little interfacial hybridization

Chemically Derived Graphenes

Reduced Graphene Oxides (RGO)

Hummers’ Oxidation

Graphite

Disperse in N,N

RGO

Limit: poor quality

CVD from Transition Metals (Cu, Ni, Pt, Ru,..)

Decomposition at T>1500°C to remove Si

Limit: high price of SiC wafer

Size limited from SiC wafer

Dehydrogenation of methane CH₄ on Copper catalytic surfaces at T=1000°C

CH₄ → C_{graphene} + 2H₂

Advantages: large area, industrially scalable, good quality

Growth from SiC

Limit: small hundreds μm-size flakes

Not scalable production
CVD Growth of Graphene

The CVD process includes the following steps:

I) Thermal ramping up in \( \text{H}_2 \)
II) Annealing in \( \text{H}_2 \) of Cu foil
III) Deposition using \( \text{CH}_4 \)
IV) Cooling down

All these steps determine graphene quality.

**Growth Conditions**
- \( \text{CH}_4: \text{H}_2 \) precursors
- 1000°C
- 1 Torr

\[ \text{CH}_4 \rightarrow \text{C}_{\text{graphene}} + 2 \text{H}_2 \]

\( \text{Cu} \)

Various additional steps are involved in the transferring of graphene to glass or any other substrate. The thermal tape release method involves the etching of the Cu foil.
Properties of Graphene on Glass

- Using multiple transferring, we can produced bilayer, trilayer and four-layer graphene on glass.
- The sheet resistance decreases going from monolayer (1L), to bilayer (2L), trilayer (3L) and to four-layers (4L) stacked graphene layers, with corresponding transmittance decreasing, still being >90%.
- The table summarizes the transmittance at 550nm and the measured sheet resistance values.
- CNR-IMIP achieved sheet resistance values, indicated by stars better than data from literature.
- The sheet resistance of unintentional doped graphene is still higher than that of ITO!
Doping of Graphene: The Challenge!

- Typically, the sheet resistance, Rs, of pristine or undoped single layer CVD graphene is of the order of 1000-5000 $\Omega/\square$ — too large to for use as a transparent conductor!
- The sheet resistance can be lowered by doping graphene.
- The challenge: it is difficult to achieve doping of graphene stable in time!

$R_s = \frac{1}{ne\mu}$

Doping of Graphene

For the application of graphene in various fields, doping is one of the efficient ways because it can tailor the electrical properties of graphene. Many researchers have investigated graphene doping methods through various processes, and they could be categorized into:

- **Electrical doping**
  - *(e.g. gate-controlled doping)*

- **Wet doping**
  - *Acid Treatment* \((\text{HNO}_3)\)
  - *Metal Chloride Treatment* \((\text{AuCl}_3)\)

- **Molecular doping**

- **Chemical Doping**
  - *(e.g. Thermal treatment in NH\(_3\))*

- **Metallic cluster-induced doping** \((\text{Au, Ag, ..})\)

- **Plasma Doping**
  - *(e.g. hydrogenation, fluorination, ..)*

Sheet resistance of pristine and doped graphene using organic dopants. The data are compared with doping with \(\text{AuCl}_3\).
Example of NH$_3$ Graphene Doping

- Real time monitoring of the (a) sheet resistance ($R_{sh}$) and (b) Hall coefficient ($R_H$) for a CVD graphene transferred on glass upon ammonia (NH$_3$) exposure (500 Torr)
- The NH$_3$ exposure time determines the doping concentration and sheet resistance
- With increasing NH$_3$ exposure time the graphene changes from p-type to n-type

Graphene Compared to ITO in Devices

Graphene electrodes achieved same good performance as ITO in OLED

- Current density, power efficiency and luminance versus voltage for OLED layer stack comprising ITO or graphene bottom electrode.
- Inset shows photograph of powered graphene-based OLED at high brightness level.
- Graphene can perform better than ITO!

[J. Mayer et al. Scientific Reports 4, Article number: 5380 doi:10.1038/srep05380 (2014)]

European Smart Windows Conference, Feb. 25, 2015, Wels, Austria
Graphene for Heatable Smart Windows

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Going beyond ITO

- Graphene films synthesized by chemical vapor deposition on Cu foils, after multiple transfers and doping, show sheet resistance as low as $\sim 43$ Ohm/sq with $\sim 89\%$ transmittance, which are ideal as low-voltage transparent heaters.

- Time-dependent temperature profiles and heat distribution analyses show that the performance of graphene-based heaters is superior to that of conventional transparent heaters based on ITO.

[B. H. Kong, Nano Lett. 11, 5154 (2011)]
Graphene for Electro-Thermal Antifog Glasses

Kimberly-Clark, the global health product manufacturer, has received a patent for an anti-fogging coating for glasses, using graphene as one of its components.

US Patent Number 8398234 describes a transparent coating for optical lenses which also conducts electricity to prevent condensation.

Electrothermal performance of graphene on glass

[D. Sui et al. Small 2011, 7, No. 22, 3186]
Glass-backed graphene with specific electrolyte for voltage-tuneable transparency/opacity in an electrochromic window/device.

- The graphene surface can be switched from full transparency to a translucent or opaque darkened state within five seconds. The system is fully reversible to transparency in two seconds.

**Key benefits**

- The transparent state is completely clear due to the graphene layer.
- A voltage is only applied to switch the system, more efficiently than constant voltage systems.
- The system is tuneable; the degree of opaqueness can be adjusted by voltage.

**Applications**

- Reduction of solar glare in windows and mirrors.
- Improved temperature and light control in buildings.
- For use in privacy windows in internal glass partitions in offices.
Graphene for Electrochromic Smart Glass

The graphene electrodes are encapsulating the electrolyte.

The graphene system is tuneable; the degree of opaqueness can be adjusted by voltage.

[E.O. Polat et al. Scientific Reports 4, 648 (2014)]
Graphene for Electrolyte-Free Electrochromic Devices

Further recent implementation: using graphene as electrodes and graphene quantum dot-viologen nanocomposites as electrolytes eliminating any additional electrolytes

- The use of electrolytes in an ECD system could lead to the unwanted decomposition of metal-ion containing electrochromes at high voltages. In order to combat the negative effect of electrolytes on device stability and performance, the researchers developed a flexible ECD where the electrochrome, methyl-viologen (MV\(^2+\)) is combined with electrostatically strong, conductive graphene quantum dots (GQDs). There is strong adherence between the MV\(^2+\) (cation) and GQDs (anion) as a result of strong electrostatic and π-π interactions. The resultant ECDs demonstrate stable electrochromic performance without the use of an electrolyte.

[Advanced Materials (DOI: 10.1002/adma.201401201; p. 5129)]
Conclusions

- CVD large area growth on practical substrates for device development is achieved.
- Doping is making graphene approaching ITO standards
- Graphene has many opportunities in smart windows technologies
- Smart windows including graphene are becoming a reality!

http://www.futuretimeline.net/forum/topic/1551-samsung-transparent-smart-window/
Acknowledgements

• MEM4WIN Consortium

http://www.mem4win.eu/

• Coworkers at CNR-IMIP:
  Maria Giangregorio, Giuseppe Bianco, Alberto Sacchetti

• European Commission under Grant Agreement GA 314578