Invited Paper

Graphene versus Oxides for transparent electrode applications

V.E.Sandana[a], D.J Rogers[b], F. Hosseini Teherani[b] P. Bove[a,b] & M. Razeghi[c]
[a]Graphos, 3 rue des Alouettes, 95140 Garges-Lès-Gonesse, France
[b]Nanovation, 8 route de Chevreuse, 78117 Chateaufort, France
[c]Center for Quantum Devices, Northwestern University, Evanston, Illinois, USA

ABSTRACT

Due to their combination of good electrical conductivity and optical transparency, Transparent Conducting Oxides (TCOs) are the most common choice as transparent electrodes for optoelectronics applications. In particular, devices, such as LEDs, LCDs, touch screens and solar cells typically employ indium tin oxide. However, indium has some significant drawbacks, including toxicity issues (which are hampering manufacturing), an increasing rarefication (due to a combination of relative scarcity and increasing demand [1]) and resulting price increases. Moreover, there is no satisfactory option at the moment for use as a p-type transparent contact. Thus alternative materials solutions are actively being sought. This review will compare the performance and perspectives of graphene with respect to TCOs for use in transparent conductor applications.

Keywords: Graphene, Transparent Conducting Oxides, Indium Tin Oxide, Transparent conductor applications

1. INTRODUCTION

Transparent, electrically conductive films can be made from a wide range of materials including titanium nitride, semiconducting oxides and ultra-thin coatings of metals such as silver and gold. Transparent conducting oxides (TCO) currently dominate for most industrial transparent electrode applications, however. Graphene is now being put forward as a transparent conductor (TC) game changer only eight years after its' isolation [1, 2] and the optical and electronic properties of graphene have attracted enormous research interest of late [3]. In this article, the suitability of graphene for transparent electrode applications is reviewed and contrasted to that of TCOs

2. TRANSPARENT ELECTRODES

The dominant industrial applications for transparent electrodes are flat panel displays (FPDs) and solar panels, which, combined, constitute more than 90% of the market [4]. A cost breakdown reveals that TCs represent about 5 and 10% of the overall manufacturing cost, respectively, for FPDs and solar cells [5-8].

Typical minimum requirements for transparent electrodes are an average transmittance of more than 80% over the whole visible spectrum and a resistivity of about 10^{-3} Ω.cm or less. To attain such performance, thin-film semiconductors should have a bandgap of 3eV, or above, and a carrier concentration of the order of 10^{20} cm^{-3} or higher [7]. Historically, most transparent electrodes employ n-type metal-oxide semiconductors (i.e. TCOs). TCO thin films that are in practical use as transparent electrodes are usually crystalline, although adoption of amorphous oxide semiconductors [10] is emerging.

2.1 Transparent Conducting Oxides (TCOs)

TCOs are often multifunctional (e.g. electrodes and/or templates/buffers and/or light management layers: e.g. anti-reflection coatings & light trapping layers), and their properties, thickness, positioning & form are considered integral to

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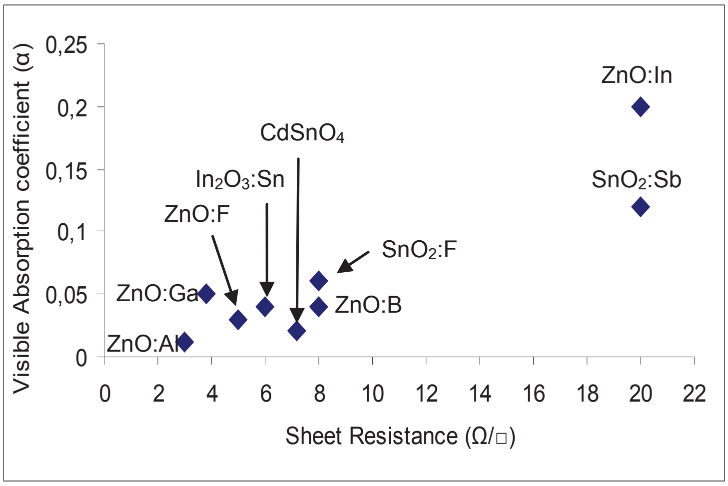
overall device design. Generally TCOs are doped oxides of tin, zinc, cadmium and their alloys (e.g: ZnO:F, ZnO:Al, CdO:Sn, CdO:In, In_2O_3:F, In_2O_3:Sn, CdO-In_2O_3, etc). [9]

Figure 1 shows a plot of two key performance parameters (visible absorption coefficient vs sheet resistance) for commonly used TCOs (adapted from [2]).



Figures 1 Typical visible absorption coefficient vs sheet resistance data for commonly-used TCOs (adapted from [9]). It should be noted that since the film thickness impacts both the visible absorption and the sheet resistance, thethicknesses of the samples here were chosen to be typical of those needed for low-resistance applications such as solar cells.

2.2 Indium Tin Oxide

In spite of the various strengths and weaknesses of the many TCOs and the range of deposition methods adopted [9-15] Indium-doped tin oxide (ITO) thin films, deposited by magnetron sputtering, are by far the most commonly used for most transparent electrode applications. Figure 2 [adapted from 16 & 17] shows a market forecast for the sales volume (in $US) of various TCOs. It can be seen that, in 2011, ITO constituted more than 90% of the transparent electrode market. This is because of the large installed production capacity combined with an acceptable cost/performance ratio.

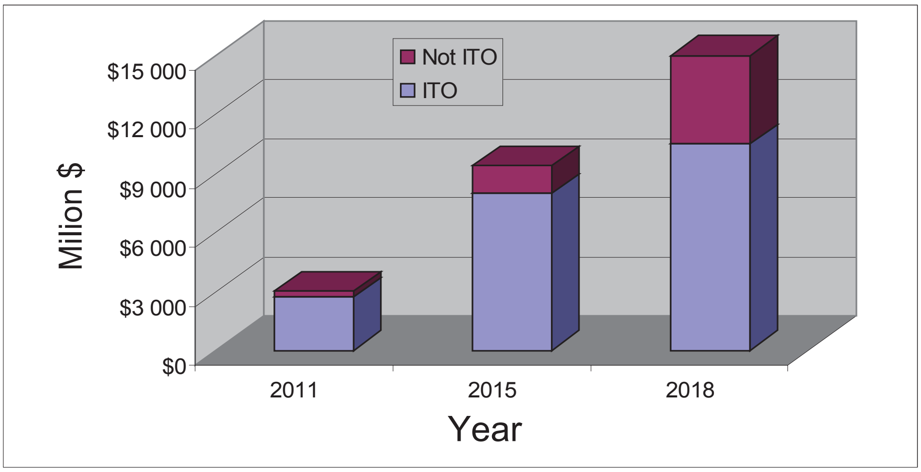


Figure 2 Forecast of the transparent conductors market from 2011 to 2018. Adapted from [16 & 17]

In 2018, the market share of ITO is forecast to drop to about 70%. This prediction is related to some drawbacks of ITO and the expected improvement in the performance/cost ratio of alternative materials. In particular, the scarcity of indium is projected to become a major problem. Indium is the 61st most abundant element in earth's crust with an average concentration of 0,24 ppm and it is used in more and more growing applications. This combination is making its' (already high) price rise. [18]. Moreover, indium-based compounds are known to be both carcinogenic and cytotoxic (they attack the heart, liver, kidneys…) [9] Furthermore, ITO is not suitable for all applications. Indeed, there is a huge diversity of applications/requirements for TCs. When factors other than transparency or conductance are paramount, other materials may offer superior solutions e.g. low cost (ITO, SnO_2:F), best resistance to H plasmas (ZnO:F), greatest thermal stability (TiN, SnO_2:F, $CdSnO_4$), highest plasma frequency (SnO:F, ZnO:F), best biocompatibility (ZnO), maximum durability (TiN, SnO_2:F) and best suitability to etching (ZnO:F, TiN) (adapted from [9]).

Additionally, other downstream considerations have to be taken into account for the choice of TCO, such as chemical stability & corrosion resistance (still a major issue for outdoor applications such as solar cells) [19]. Other potentially important selection criteria include abrasion resistance, electron work function, compatibility with substrate (& other components), appropriateness for the application, ease of manufacturability and the economics of the deposition method. Thus selection of the optimal TCO, in terms of functionality and costs, is not always straightforward.

3. TCs: NEW DEVELOPMENTS

It has been over a hundred years since K. Baedeker, [20] reported the first TCO: CdO. With the rapid development since the 1970s of ZnO, SnO_2 and In_2O_3 based TCc, [21] TCOs have become a mature technology with relatively little advance in recent years. In order for transparent electrode performance to make significant further improvements, a new paradigm is probably needed. Some possible candidates for this are conductive polymers, new hybrids/composites, superconductors, nanostructures and (the subject of this paper) graphene

According to the pioneers (A.K Geim and K.S. Novoselov [22]), graphene is *"the mother of all graphitic forms"* Indeed, graphene is a like 2D building material for carbon materials of all other dimensionalities. For instance, it can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite. Since 2004, the interest for this new material has skyrocketed, with a compound annual growth rate (CAGR) of related publications in excess of 36% from 2004 to 2012 (based on data from Wiley Publications, ACS Publications, Nature, AIP & Springer Link).

Table 1 summarizes some of the key properties of state-of-the-art graphene:

Hexagonal structure	a1=a1=2.46 Å
Transmittance	97.7% in visible spectrum
Low resistivity	~30 Ω/□
Mobility	200 000 cm²/V.s
Thermal Conductivity	5000 W·m−1·K−1
Melting Point	3948.15 K
Band gap engineering	Metallic / Semiconductor

Table 1 Some key properties of state-of-the-art graphene (Adapted from [3, 22])

Graphene, however, is not limited to such fixed properties, however. One of the most interesting aspects of graphene is its' highly tuneable bandgap, which provides it with the flexibility to be either metallic or semiconducting. Indeed, the number of publications related to "doped graphene" has increased rapidly over the last 4 years, outstripping the CAGR for graphene as a whole .[23] There is still much work to be done, though. Some current graphene issues are the non-availability of a wide-area uniform production tool, the tendency to form Multi Layer Graphene (MLG) or incomplete layers (rather than Single Layer Graphene (SLG)) , "wrinkles" (which severely impact the properties), wear resistance and oxidation.

3.1 Graphene growth processes

3 main categories of fabrication process have emerged for graphene: dry exfoliation, direct deposition and chemical exfoliation. [24] According to Nanotech Insights [25], 13 mains growth tools for graphene have been patented. The survey records 241 patents among which, 94 are for exfoliation and 92 are for Chemical Vapor Deposition (CVD). Together, these two techniques represent almost 80% of the patented processes.

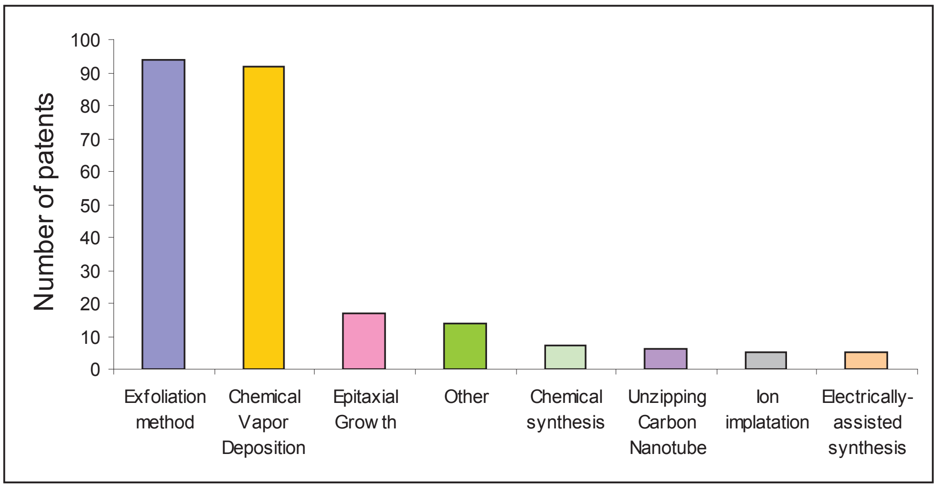


Figure 3 Number of graphene synthesis method patents (adapted from [25]).

3.1.1 Dry exfoliation:

"Scotch tape" fabrication (illustrated in figures 4 and 5) was the first technique used for graphene isolation It is an example of dry mechanical exfoliation (or Micromechanical Highly Oriented Pyrolytic Graphite cleavage). This relatively simple process allowed the first synthesis of SLG. Excellent crystalline quality can be obtained with this method and fundamental study of graphene can thus easily be made in laboratory. The approach has proven to be of limited scalability, however, and it is generally considered to be unsuitable for industrial production [24]

3.1.2 Chemical Vapor Deposition (CVD)

The most studied process for obtaining wide area samples of graphene is CVD. In this approach (Figure 5c) a hydrocarbon precursor is direct towards a copper substrate.

The growth mechanism is based on the decomposition of the incident hydrocarbons when they arrive at the heated substrate such that carbon nucleates on the Cu and the nuclei then grow into relatively large domains [25-26]. The nucleation density has been found to be a function of pressure and temperature [25-26]. At relatively high temperature (T>1000°C) and low precursor pressure (mTorr range), relatively large (~0.5 mm) single crystal domains form. Once the Cu surface is fully covered, the films become polycrystalline, since the nuclei are not coherently registered [25-26] i.e. they are mis-oriented with respect to each other (even if nucleated on the same Cu grain). It has been suggested that this could be ascribed to a relatively low Cu-C binding energy. [27]. The compatibility of CVD with current chip fabrication and the self-limiting nature of the process [24] (i.e. CVD growth practically ceases when the Cu surface is fully covered with graphene) are very promising for CVD mass production. The main drawbacks, currently, are the expensive copper substrate and the relatively poor crystalline quality that is generally obtained. [24]

3.1.3 Wet exfoliation

A wet chemical dispersion of graphene flakes can be produced by ultrasonication of graphite in water [28-29] or organic solvents [30-31] (Figure 5b). Such "wet exfoliation" functions via the formation, growth, and collapse of bubbles (or voids) in the liquid due to pressure fluctuations: "Cavitation". Hydrodynamic shear-forces associated with cavitation cause the graphite to exfoliate into flakes. The solvent-graphene interaction needs to be adapted so as to balance the inter-sheet attractive forces. This process is low cost, but the relatively small size of the graphene flakes is not adapted for the mass electronic market.

Figure 4 Cleaving graphite with scotch tape in order to obtain graphene.

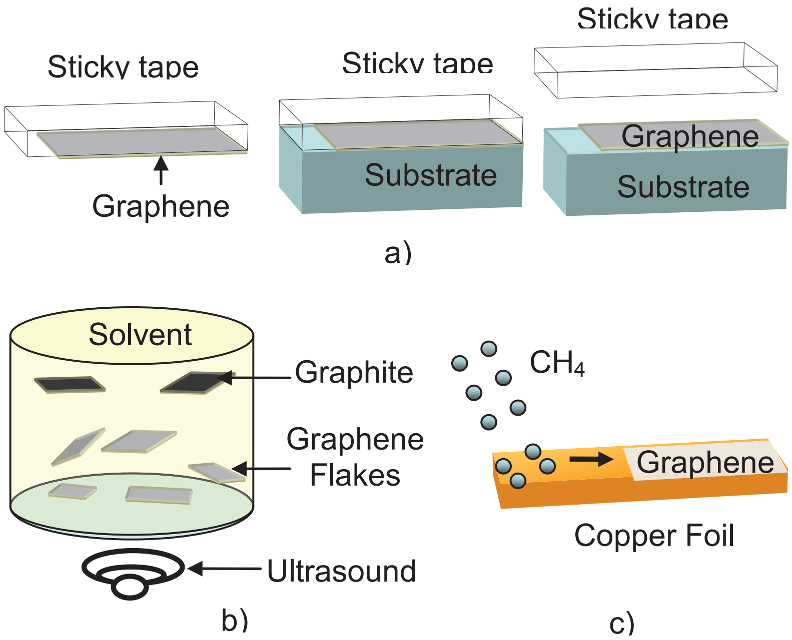


Figure 5 Schematics of the a) scotch tape technique used to transfer graphene onto a substrate b) CVD process c) ultrasonication of graphite.

4. GRAPHENE VS TCOs FOR N-TYPE TRANSPARENT CONDUCTOR APPLICATIONS

Recently there has been a lot of research targeted at replacing TCOs by graphene for transparent electrode applications. A comparison of some key properties of state-of-the-art graphene and ITO TCs is given in table 2.

Material	Resistance Ω/□	Visible Spectrum Transparency	Cost	Production Data	Robustness
Graphene	30-280	97.7%	$ 5000/m²	Continuous 800 mm wide sheet *	☺ ☺ ☺?
ITO	30-80	90%	$ 7/m²	14 000 ksqm In 2012	☺

* not really yet

Table 2 Properties comparison between ITO and state-of-the-art graphene for n-type transparent electrode applications (adapted from [3, 9, 24, 32]). Of particular note is that graphene has a distinct intrinsic transparency advantage over ITO (and TCOs in general).

Figure 6 shows a plot comparing two key parameters (Transmittance vs Sheet resistance) for state-of-the-art graphene and ITO (adapted from the data of [3, 9, 24, 32]). The graphene shows a continually improving conductivity and an already superior transmittance compared to ITO. The exorbitant current cost of graphene per m² compared to ITO is expected to decrease dramatically due to the huge research effort currently targeting improved mass production. [30-31]. The ITO price, on the other hand, will remain stable or increase due to the aforementioned indium scarcity and increasing demand. [1]

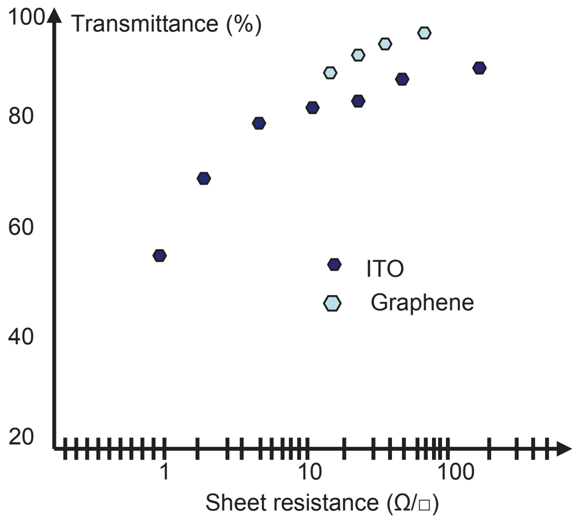


Figure 6 Transmittance vs sheet resistance for state-of-the-art Graphene & ITO (adapted from [3, 9, 24, 32]).

Highly flexible and transparent graphene films obtained by CVD have already been successfully demonstrated for use as transparent electrodes in organic photovoltaic cell prototypes. [32] Moreover, Gomez de Arco et al. [33] demonstrated the outstanding capacity of CVD graphene solar cells to operate reproducibly after repeated bending at angles of up to 138° (as compared to ITO-based devices which displayed cracks and irreversible failure under bending of 60°). This indicates a great potential of CVD graphene films for flexible PV applications. Bae et al. demonstrated the successful adoption of graphene as a replacement for ITO electrodes in FPDs. [32] Moreover they developed this using a roll-to-roll process which shows much promise for low cost mass production of graphene. A 30 inch diameter graphene foil was obtained via a process which included transfer to a host substrate (after the CVD) via chemical dissolution of the Cu and dry transfer-printing.

5. P-TYPE GRAPHENE

The first p-type TCO emerged relatively recently, with the synthesis of p-type $CuAlO_2$ in 1997 [34]. Subsequently, a wide range of p-type TCOs has been developed (for instance Cu_2O, SnO, $CuAlO_2$, $CuGaO_2$, $SrCu_2O_2$, NiO, Spinels, MoO_3 etc. can all be p-type) but they are at a fairly early stage of development (i.e. mobility, carrier concentration and conductivity are still way too low for most transparent conductor applications) compared with n-type TCOs and the perspectives remain unclear. One of the most interesting contributions expected from graphene is the emergence of a new candidate for use as a p-type transparent conductor. Indeed, it has already been shown that transparent graphene can be doped so as to exhibit p-type behaviour. [23] For instance, graphene is p-doped by simply oxidizing with a strong acid. [35] Moreover, it is possible that such chemical-based p-type doping could be integrated into the roll-to-roll fabrication process in order to mass produce p-type transparent electrodes.

6. INDUSTRIAL ADOPTION OF GRAPHENE

The pie charts in figure 7 show a forecast of the evolution of the various graphene market sectors (adapted from [16]). From 2015 to 2020 the value of the graphene market as a whole is projected to grow by a factor of 10. According to BBC research, transparent electrodes (in both PVs and FPDs) will be key early markets for graphene. The PV market for graphene transparent electrodes is already predicted to be worth $ 7.37 million in 2 years from now and the FPD application will be a strong emerging sector for graphene-based electrodes.

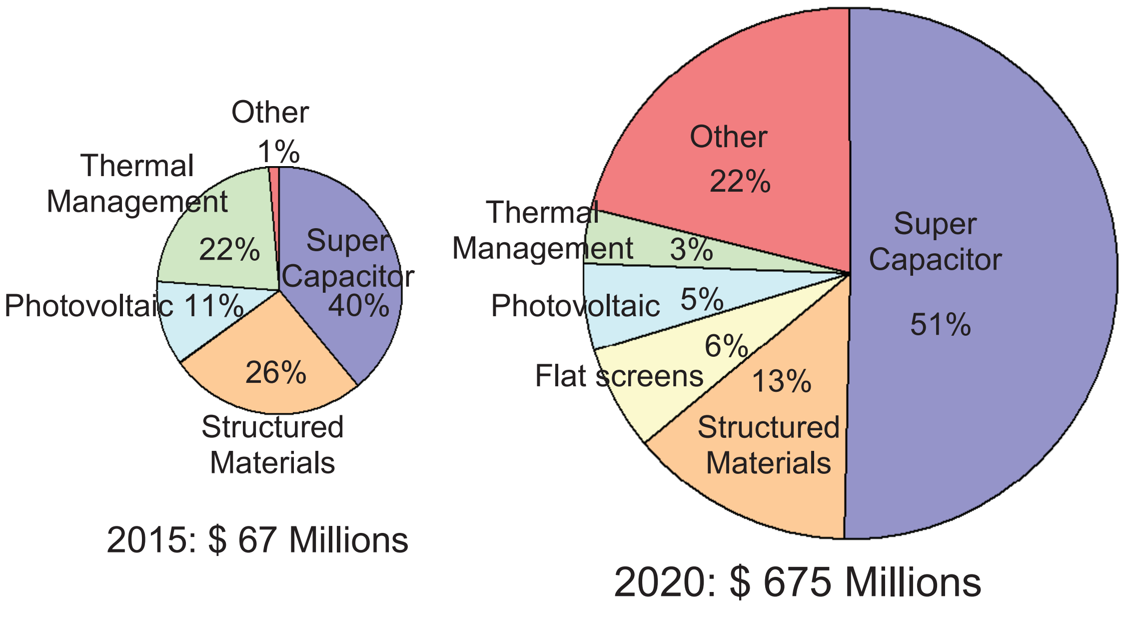


Figure 7 Graphene market evolution 2015-2020 (adapted from [16]).

7. CONCLUSION

Among the various TCOs, ITO is still considered to offer the best optical/electrical/cost compromise for transparent electrode applications and dominates the market. Other materials are emerging, however, as toxicity legislation & a continually degrading supply/demand ratio for indium turn the screw on ITO. Graphene is a relatively new arrival on the transparent electrode scene but it already shows superior transparency & adequate conductivity. Graphene currently has significant production issues, however, & the cost levels are too high. Both of these are evolving rapidly though and functioning PV/FPD prototypes suggest that roll-to-roll CVD could well rise to the challenge. Thus graphene is considered a very promising candidate for ITO replacement in the medium term. For p-type TC applications, it would also seem that graphene is a top contender and that future development may well be based on wet chemical oxidation.

REFERENCES

[1] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V;, Grigorieva, I. V. and Firsov, A. A., "Electric Field Effect in Atomically Thin Carbon Films," Science 306(5696), 666-669 (2004).

[2] Dresselhaus, M. S., Araujo, P. T., "Perspectives on the 2010 Nobel Prize in Physics for Graphene," ACS Nano 4, 6297-6302. (2010).

[3] Bonaccorso, F., Sun, Z., Hasan, T. and Ferrari, A. C., "Graphene Photonics and Optoelectronics", Nature Photon 4, 611-622 (2010).

[4] Glen, A., "Indium Tin Oxide and Alternative Transparent Conductor Markets", NanoMarket LC (2009).

[5] Colegrove, J., " LCD In-cell Touch," Info. Display Mag. 26(3), 8-14 (2010).

[6] Kalowekamo, J. and Baker, E., "Estimating the manufacturing cost of purely organic solar cells," Sol. Energy 83 (8), 1224-1231 (2009).

[7] Minami, T., "Transparent conducting oxide semiconductors for transparent electrodes," Semicond. Sci. Technol. 20, 35-44 (2005).

[8] Coutts, T. J., Young, D. L. and Li, X., "Characterization of Transparent Conducting Oxides," MRS Bull. 25(8), 58-65 (2000)

[9] Gordon, R. G., "Criteria for Choosing Transparent Conductors," MRS Bull. 25(8), 52-57 (2000).

[10] Rogers, D.J., Sandana, V. E., Teherani, F. H., McClintock, R., Razeghi, M. and Drouhin, H.-J., "Amorphous ZnO films grown by room temperature pulsed laser deposition on paper and mylar for transparent electronics applications," Proc. SPIE 7940, 79401, K1-K8 (2011).

[11] Dawar, A. L. and Joshi, J. C., "Semiconducting transparent thin films: their properties and applications," J. Mater. Sci. 19(1), 1-23 (1984)

[12] Chopra, K. L., Major, S. and Pandya, D. K., "Transparent conductors—A status review," Thin Solid Films 102 (1), 1-46 (1983)

[13] Hartnagel, H. L., Dawar, A. L., Jain, A. K. and Jagadish, C., [Semiconducting Transparent Thin Films], Institute of Physics Publishing, Philadelphia (1995).

[14] Minami, T., "New n-Type Transparent Conducting Oxides," MRS Bull. 25(8), 38-44 (2000)

[15] Freeman, A. J., Poeppelmeier, K. R., Mason, T. O., Channg, R. P. H. and Marks, T. J., "Chemical and Thin-Film Strategies for New Transparent Conducting Oxides," MRS Bull. 25(8), 45-51 (2000)

[16] McWilliams, A., "Graphene: Technologies, applications and markets," BCC Research, AVM075B (2011)

[17] Allen, G., "NanoMarkets predicts entire transparent conductor market to reach 5.6 billion dollars in 2015," Azonano, 13 June 2012, http://www.azonano.com/news.aspx?newsID=18021

[18] "The indium market and compound semiconductors," Compound Semiconductor, 23 Sep, 2003, http://www.compoundsemiconductor.net/csc/features-details.php?cat=features&id=18194

[19] Jansen, K. W. and Delahoy, A. E., "A laboratory technique for the evaluation of electrochemical transparent conductive oxide delamination from glass substrates," Thin Solid Films 423(2), 153-160 (2003).

[20] Baedeker, K., "Uber die elektrische Leitfähigkeit und die thermoelektrische Kraft einiger Schwermetallverbindungen," Ann. Phys. 22, 749–766 (1907).

[21] Haacke, G., "Transparent conducting coatings," Ann. Rev. Mater. Sci. 7, 73 (1977).

[22] Geim, A.K. and Novoselov, K. S., "The rise of graphene," Nature Materials 6(3), 183-191 (2007).

[23] Lv, R. and Terrones, M., "Towards new graphene materials: Doped graphene sheets and nanoribbons," Materials Lett. 78, 209-218 (2012).

[24] Bonaccorso, F., Lombardo, A., Hasan, T., Sun, Z., Colombo, L. and Ferrari, A. C., "Production and processing of graphene and 2d crystals," Materials Today 15(12), 564-589 (2012).

[25] Sivudu, K. S. and Mahajan, Y., "Mass production of high quality graphene: An analysis of worldwide patents, " Nanowerk 28 June, (2012), http://www.nanowerk.com/spotlight/spotid=25744.php
[26] Li, X., Magnuson, C. W., Venugopal, A., An, J., Suk, J. W., Han, B., Borysiak, M., Cai, W., Velamakanni, A., Zhu, Y. Fu, L., Vogel, E. M., Voelkl. E., Colombo, L. and Ruoff, R. S, "Graphene Films with Large Domain Size by a Two-Step Chemical Vapor Deposition Process," Nano Lett. 10(11), 4328-4334 (2010)
[27] Li, X., Magnuson, C. W., Venugopal, A., Tromp, R. M., Hannon, J. B., Vogel, E. M., Colombo, L. and Ruoff, R. S.,"Large-Area Graphene Single Crystals Grown by Low-Pressure Chemical Vapor Deposition of Methane on Copper, " J. Am. Chem. Soc. 133(9), 2816-2819 (2011)
[28] Hernandez, Y., Nicolosi,F., Lotya, M., Blighe, F. M., Sun, Z., De, S., McGovern, I.T., Holland, B., Byrne, M., Gun'Ko, Y. K., Boland, J. J., Niraj, P., Duesberg, G., Krishnamurthy, S., Goodhue,R., Hutchison, J., Scardaci, V., Ferrari, A. C. and Coleman, J. N., "High-yield production of graphene by liquid-phase exfoliation of graphite," Nature Nanotech. 3, 563-568 (2008).
[29] Maragó,O. M., Bonaccorso, F., Saija, R., Privitera, G., Gucciardi, P. G., Iatì, M. A., Calogero, G., Jones, P. H., Borghese, F., Denti, P., Nicolosi, V. and Ferrari, A. C, "Brownian Motion of Graphene," ACS Nano 4(12), 7515-7523 (2010).
[30] Lotya, M., Hernandez, Y., King, P. J., Smith, R. J., Nicolosi, V., Karlsson, L. S., Blighe, F. M., De, S., Wang, Z., McGovern, I. T., Duesberg, G. S. and Coleman, J. N., "Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions," J. Am. Chem. Soc. 131, 3611 (2009).
[31] Blake, P., Brimicombe, P. D., Nair, R.R., Booth, T. J., Jiang, D., Schedin, F., Ponomarenko, L. A., Morozov, S. V., Gleeson, H. F., Hill, E. W., Geim, A. K, Novoselov. K. S., "Graphene-based liquid crystal device," Nano Lett. 8, 1704-1708 (2008).
[32] Bae, S., Kim, H., Lee, Y., Xu, X., Park, J.-S., Zheng, Y., Balakrishnan, J., Lei, T., Kim, H.R., Song, Y. I., Kim, Y.-J., Kim, K.S., Özyilmaz, B., Ahn, J.-H., Hong, B. H. and Iijima, S., "Roll-to-roll production of 30-inch graphene films for transparent electrodes," Nature Nanotech. 5, 574-578 (2010).
[33] Gomez De Arco, L., Zhang, Y., Schlenker, C. W., Ryu, K., Thompson, M. E. and Zhou, C., "Continuous, Highly Flexible, and Transparent Graphene Films by Chemical Vapor Deposition for Organic Photovoltaics," ACS NANO 4 (5), 2865–2873 (2010).
[34] Kawazoe, H., Yasukawa, M., Hyodo, H., Kurita, M., Yanagi, H. and Hosono, H., "P-type electrical conduction in transparent thin films of $CuAlO_2$," Nature 389, 939-942 (1997).
Chen, D., Feng, H. and Li, J., "Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications," Chem. Rev. 112, 6027−6053 (2012).