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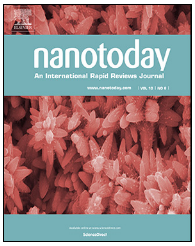

REVIEW

Challenges and opportunities for graphene as transparent conductors in optoelectronics

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Summary As optoelectronic devices become more ubiquitous and applications for such devices begin to diversify, there is an increasing demand for an alternative transparent conducting film to address the shortcomings of transparent metal oxides. Graphene, which combines excellent optical transparency with mechanical robustness and chemical inertness, is a strong candidate for this purpose. Synthesize techniques such as chemical vapor deposition and liquid phase exfoliation allows researchers to produce large-area transparent conducting films that can be used for devices such as solar cells and light-emitted diodes. However, practical issues such as insufficient conductivity or surface roughness from transfer often hamper device performance. Nonetheless, researchers have succeeded in demonstrating graphene electrode-based solar cells, LEDs, photodetectors, and lasers. In this review, we present an overview of progress made in building optoelectronic devices with graphene as the transparent conductor and identify the major challenges that must be overcome before the material can move from the laboratory to industry.

Introduction and background

Graphene is a two-dimensional array of carbon atoms arranged in a planar hexagonal configuration. Over the past decade, the material has attracted enormous attention from researchers due to its remarkable physical and chemical characteristics. From an optoelectronics standpoint, graphene is both electrically conductive and optically transparent — a pair of properties rarely found together — making it a natural candidate for next-generation transparent conductors (TCs). Currently the TC market is dominated by conductive metal oxides such as indium tin oxide (ITO), fluorine-doped tin oxide (FTO), and aluminum-doped zinc oxide (AZO). Of these, ITO offers the best conductivity. However, it has the drawback of being expensive because indium

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is a rare earth metal primarily found in zinc deposits and is therefore produced in small quantities as a by-product. To address increasing demand, researchers have been exploring the possibility of applying other materials such as metal grids/nanowires, carbon nanotubes (CNTs), conductive polymers, and graphene.

All of the emerging technologies listed above have potential advantages over ITO in certain respects such as conductivity, flexibility, or cost. Metal grids offer excellent conductivity and good optical transmittance but require patterning via photolithography or shadow mask evaporation. More recently, researchers developed other types of metallic networks such as spin-on silver nanowires or metallic 'nanotroughs'. Disadvantages include higher cost, greater surface roughness, instability in air due to oxidation, and hazing. We refer the reader to other review articles for detailed discussions [1—3]. Carbon nanotubes can, in some ways, be thought of as the predecessor to graphene. CNT transparent conducting films are approaching realization in industry; in fact, companies have demonstrated working touch screens using carbon nanotube films. However, synthesis and purification of high quality nanotubes can be difficult and like nanowires, nanotube films have higher surface roughness, which is undesirable for some applications [4,5]. Conducting polymers such as PEDOT:PSS have also shown promise. Normally, the conductivity of these polymers is very low compared to ITO. Simple modifications such as dipping in alcohol can enhance the conductivity significantly, but still lower than other TCs. PEDOT:PSS can also be deposited over large areas by spin-coating, printing, or oxidative chemical vapor deposition. As before, we refer to other comprehensive reviews for more information on the topic [6,7]. These emerging technologies are very different, each having advantages and disadvantages that constantly evolve as research progresses rapidly. In this review, we focus our attention on graphene.

The atomic arrangement of carbon atoms in graphene gives rise to unique electrical properties. The delocalized π-electrons have mobility values as high as 200,000 $cm^2/V\,s$ at room temperature, resulting in intrinsic resistivity as low as 30 Ω/sq [8]. The theoretical optical absorption of graphene — 2.3% per layer — is determined by the fine structure constant, which describes the coupling between light and relativistic electrons [9]. These theoretical values for sheet resistance and optical transmittance compare favorably to carbon nanotubes films and conductive polymers. Furthermore, graphene films are uniform with atomically flat surfaces and can be cheaper to synthesize than metal grids or nanowires. In spite of these advantages, when comparing graphene to ITO, many researchers are skeptical about graphene's prospects of becoming the dominant TC. History has shown that older, established technologies are difficult to displace, and ITO is indeed a well-entrenched industry standard. Efforts have also been made to recover indium from used electronics such as LCD panels to alleviate the resource demand [10]. However, at present, ITO has mostly been used in applications with flat, rigid substrates. Recently, bendable or curved devices have become an emerging trend, where the flexibility of graphene may play a key role. Furthermore, other advantages of graphene open possibilities for technologies that may not be compatible with ITO. For example, ITO cannot be used in dye sensitized solar cells because the sintering process during fabrication requires the TC to survive temperatures upwards of 400 °C. Similarly, in organic photovoltaic devices (OPVs), ITO has been shown to degrade over time, resulting in reduced performance and lifetime [11,12]. In contrast, graphene has remarkable thermal stability and chemical inertness, making it a promising candidate for these applications. In addition, it is anticipated there will be increased demand for TCs in the future, so the cost and abundance of graphene may become more important.

Because graphene is still a relatively new material, researchers take different approaches in trying to make it more industrially relevant. One approach is to improve the physical properties of the graphene itself. While the theoretical properties of graphene, such as its atomic flatness and high electrical conductivity, are highly attractive, it is often difficult to achieve such results in practice. Thus, much of the community's efforts focuses on making graphene more attractive by bridging the gap between theory and practice, for example: controllably synthesizing large-area defect-free films, improving the sheet resistance by surface modifications, or developing transfer processes that allows the growth substrates to be recycled. Many of these efforts are described in section 2-graphene synthesis and processing. Another approach is to use graphene for existing technologies in place of conventional TCs to assess the advantages and disadvantages of the material. For example, researchers have demonstrated flexible organic solar cells and LEDs using graphene electrodes with performance similar to or exceeding that of ITO-based devices. At this stage, these investigations are quite preliminary and many aspects such as device reliability and reproducibility have not yet been thoroughly investigated. Specific results are summarized in section 3 of this review — optoelectronic devices with graphene electrodes.

Graphene synthesis and processing

Synthesis of large-area graphene

In 2004, graphene was first isolated by mechanically exfoliating from graphite flakes — a process colloquially known as 'scotch-taping' (Fig. 1a) [13]. Unfortunately, the size of the exfoliated flakes was limited to hundreds of microns, which meant that fabricating large-scale optoelectronic devices were not possible using mechanically exfoliated graphene. However, researchers soon developed scalable methods of preparing large-area film — the most common of which are chemical vapor deposition (CVD) and liquid phase exfoliation. We briefly discuss these two methods.

Chemical vapor deposition

CVD is a bottom-up synthesis method that generally produces continuous films with sheet resistances of a few hundred Ohms per square and optical losses very close to the ideal 2.3% per layer, which makes it very popular amongst research communities. In a typical CVD process, the growth substrate (most commonly copper foil or nickel thin film) is annealed at high temperatures (~1000 °C) in a reducing environment. After annealing, a carbon source such as methane is introduced into the growth chamber. The high