Microwave-assisted boron and nitrogen co-doped reduced graphene oxide as a transparent conductive electrode

Sima Umrao,[1] Himanshu Mishra,[2] Anchal Srivastava,[2] and Sungjoo Lee[1,3,a)]
[1]*SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon 440-746, South Korea*
[2]*Department of Physics, Institute of Science, Banaras Hindu University (BHU), Varanasi 221005, India*
[3]*School of Electronics and Electric Engineering, Sungkyunkwan University (SKKU), Suwon 440-746, South Korea*

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A crystalline Boron (B)- and Nitrogen (N)-co-doped microwave-assisted reduced graphene oxide (BNMRGO) film was investigated as a potential transparent conducting electrode (TCE) material. X-ray diffraction results revealed the good crystallinity of the BNMRGO film, and the presence of a (0004) reflection plane indicated the formation of a few small domains of hexagonal boron nitride in the microwave assisted reduced graphene oxide (MRGO) sheets under the co-doping process. Raman and X-ray photoelectron spectroscopic results indicated a reduction of sp^3 carbon centers upon co-doping. The I_D/I_G ratio decreased after co-doping from 0.89 to 0.24, indicating a low average defect density of $\sim 1.01 \times 10^{10}\,cm^{-2}$. Optoelectronic characterization of the BNMRGO film on a glass substrate revealed a high optical transparency of 82% at 550 nm and a low sheet resistance (R_{sh}) of 355 Ω/sq, which was lower than that observed from the MRGO sheets ($R_{sh} = 719\,\Omega/sq$). BNMRGO provided a ratio between the direct conductivity (σ_{dc}) to the optical conductivity (σ_{oc}), that is, the figure of merit of a TCE material, of 5.96. Overall, this work paves the way toward developing a manufacturable TCE. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4993156]

Transparent conducting electrodes (TCEs) with a high optical transparency (T), low sheet resistance (R_{sh}), and appropriate work function are critical component of optoelectronic devices, including touch screens, organic solar cells, and organic light emitting devices (OLED). Most common TCEs use indium tin oxide (ITO) with a low $R_{sh} = 10$–$30\,\Omega/sq$. Although ITO displays a transmittance of 90%, it is not flexible, incurs high production costs, and is typically deposited via high-temperature processes.[1] Moreover, next-generation flexible organic optoelectronic devices may require TCEs with a high work function compatible with that of an organic semiconductor to facilitate charge injection/collection. Unfortunately, ITO is characterized by a low work function (4.3–4.7 eV).[2] Researchers have studied a variety of materials as potential alternatives to ITO, including conducting polymers, metals, and carbon-based nanostructures.[3,4] Graphene recently showed promise for use as a TCE material in both stiff and flexible devices.[1,3] Recently, Ahn *et al.*[5] developed a method for synthesizing large-area graphene films with an R_{sh} of 125 Ω/sq and a 97.4% transmittance via a roll-to-roll chemical vapor deposition (CVD) process on a copper foil support. Solution processing can be used to synthesize a graphene film by directly depositing natural graphite flakes onto graphene.[6,7] This method has attracted attention as a facile film deposition method compatible with arbitrary substrates and capable of depositing a scalable quantity of graphite flakes using a simple coating method, such as spin coating, dip coating, or spray coating.[1,8] reduced graphene oxide (RGO)-based thin films manufactured over large scales and at low cost are appealing for use in the manufacture of next-generation flexible electrodes[9] and printable substrates.[10] A variety of studies have reported the fabrication of RGO-based TCEs with a range of R_{sh} values (200–700 kΩ/sq) with a range of transmittance values (40%–92%), as noted by Xue *et al.*[11] Lattice and surface defects are present in RGO because of the presence of functional groups and impurities created during the process of chemical oxidation. Such defects create undesirable electrical properties.[12] The chemical and electronic properties of RGO may be moderated in a well-controlled manner by adjusting the reduction level and degree of heteroatom doping. Recently, RGO was synthesized by reducing GO using microwave irradiation without a reducing agent. The resulting films showed better conductivities than the chemically and thermally reduced GO,[13–15] although the conductivity was 21 $S\,m^{-1}$ and did not meet the relevant technical requirements.[16] A variety of groups have developed N-doped RGO-based TCEs for use in OLEDs with R_{sh} values in the range of 298–1100 Ω/sq at a transmittance of 60%–90%;[9,17] however, heteroatom-doped RGO showed a higher conductivity than RGO,[16] as well as an enhanced pseudo-capacitance.[18] The high sheet resistance and low transparency may have been due to the presence of defects and impurities in the RGO.

In this work, we synthesized, *in-situ*, Boron (B)- and Nitrogen (N)-co-doped microwave-assisted reduced graphene oxide (BNMRGO) with a high percentage of doping using a one-step microwave-assisted method[19,20] without the use of toxic reducing agents. GO reduction and doping, and the formation of small hexagonal boron nitride (*h*-BN) domains, took place simultaneously, as schematically described in Fig. 1(a). The process is described in detail in the experimental section of the supplementary material. The diffraction peak

a)Author to whom correspondence should be addressed: leesj@skku.edu. Telephone: +821045970413.

Self attested
Himanshu