

## GRAPHENE-BASED TRANSPARENT CONDUCTIVE FILMS

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Graphene is a promising alternative to indium tin oxide for use in transparent conducting electrodes. We review recent progress in production methods of graphene and its applications in optoelectronic devices such as touch panel screens, organic photovoltaic cells, organic light emitting diodes and thin film transistors. In addition, we discuss important criteria such as optical transmittance, electrical conductivity and work function, which are critical considerations in the integration of graphene conductive films with optoelectronic devices.

Keywords: Graphene; transparent electrodes; organic devices; thin film transistor.

#### 1. Introduction

There have been numerous reports of scientific and technical advances in graphene research since its two-dimensional form was successfully isolated on a substrate by Geim and Novoselov.<sup>1–3</sup> Interesting characteristics stemming from its two-dimensional geometry have been observed by a number of researchers. Some fascinating characteristics include a high carrier mobility ( $\sim 200\,000\,\mathrm{cm}^2/\mathrm{Vs}$ ),<sup>1</sup> outstanding optical transparency ( $\sim 97.7\%$ ),<sup>4</sup> and a high Young's modulus ( $\sim 1.0\,\mathrm{TPa}$ ).<sup>5</sup> These extraordinary properties of graphene have led to interest in using it for real applications.

Among many possible applications, graphene has been studied in the field of transparent electrodes due to its potential to satisfy the requirements of various devices. Recent thin film technology for transparent conductive film has been developed to solve several issues (1) improvement of electrical conductivity (2) enhancement of mechanical flexibility (3) reduction of material cost.<sup>6,7</sup> Indium tin oxide (ITO) has been widely used in many applications because of its low sheet resistance of  $10-25 \Omega/sq$  at 90% transmittance and simple deposition process by sputtering.<sup>6</sup> However, it has many obstacles which include the scarcity of indium

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on earth, difficulty in the fabrication steps and poor mechanical flexibility.<sup>6,7</sup> It also has poor electrical contact with organic materials that can limit the performance of organic electronic devices such as organic light emitting diodes (OLEDs), organic photovoltaic cells (OPVs) and organic transistors. Therefore, many researchers have been seeking alternative materials to overcome such drawbacks.

Table 1 shows properties of representative materials of a new class for transparent conductive films. Poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films have advantages in terms of production cost and mechanical properties, but they possess poor stability under environmental condition.<sup>8–10</sup> Silver nanowire films can achieve good electrical conductivity and optical transmittance.<sup>11</sup> However, it needs strong acid treatment and protection layer in order to prevent oxidation.<sup>11,12</sup> Carbon nanotube (CNT) films have a limitation of sheet resistance due to high contact resistance between nanotube bundles, although they exhibit outstanding mechanical property (failure tensile strain over 11%).<sup>13</sup> As an alternative, graphene has attracted lots of attention due to relatively low sheet resistance ( $\sim 35 \Omega/sq$  at 90% optical transmittance), great mechanical flexibility, possibility of low manufacturing cost based on roll-to-roll method and a plentiful supply of raw materials.<sup>7,14–16</sup>

In this paper, we introduce some promising routes for the fabrication of large-area graphene films by the reduction of graphene oxide flakes and chemical vapor deposition. In addition, several applications of graphene-based transparent conductive films such as touch screens, optical devices and carbon-based thin film transistors (TFTs) are presented to demonstrate the utility of graphene for future electronic applications.

### 2. Transparent Conductive Graphene Film

#### 2.1. Large-area graphene film synthesis

Graphene films have been fabricated by various methods such as mechanical exfoliation,<sup>2,3</sup> high temperature annealing of SiC,<sup>17</sup> chemical reduction of graphene oxide<sup>18–22</sup> and chemical vapor deposition.<sup>23–25</sup> The productivity and properties depend on the preparation method. Although the pristine properties of graphene are preserved in mechanical exfoliation, the productivity is inadequate because the resulting area of produced graphene is only on the micrometer scale. Furthermore, graphene formed on a SiC substrate cannot be transferred to an arbitrary substrate. For this reason, chemical reduction of graphene oxide and chemical vapor deposition (CVD) have been intensively researched in order to produce large-area graphene films.<sup>14,22,25,26</sup>

In order to fabricate reduced graphene oxide (rGO), graphite oxide should be dispersed in solution. Figure 1(a) shows a scheme for rGO fabrication.<sup>19</sup> Once the graphite is prepared, graphite oxide can be formed using an oxidizing agent such as concentrated acid. Hummer and Offeman described an oxidation method employing a solution of sodium nitrate, potassium permanganate and concentrated sulfuric acid.<sup>22</sup> This method has been most commonly used to oxidize graphite. The graphite oxide obtained using this method has strong hydrophobic properties, which yields an increased distance between layers of up to  $0.6-1.2\,\mathrm{nm}$ . Due to the increased layer distance, graphene oxide flakes can be exfoliated by sonication. Graphene oxide chemically exfoliated by this method involves hydroxyl and epoxy groups on platelets and carboxyl groups at the edges, resulting in the loss of pristine graphene film properties. Nevertheless, graphene oxide flakes can be converted to rGO by a reduction

Table 1. Properties of various materials for transparent conducting film.

	Thickness (nm)	Transparency (%)	Sheet resistance (Ω/sq)	Failure strain (%)	Cost	ref
ІТО	100~200	> 90	10~25	1.4	120 \$/m <sup>2</sup>	6, 7
PEDOT:PSS	15~33	80~88	65~176	3~5	2.3 \$/ml	8,9,10
Silver NWs	~ 160	92	100	~1.2	40 \$/m <sup>2</sup>	11,12
CNT	7	90	500	~ 11	35 \$/m²	13
Graphene	0.34	90	~ 35	~7	45 \$/m²	1,4,14



Fig. 1. Mechanism of graphene synthesis (a) Synthesis steps of graphene by reduction of chemically exfoliated graphene oxide. (b) Graphene growth by CVD with metal catalyst. (c) and (d) Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of graphene film grown by CVD process. Reproduced with permission from 23. Copyright (2009), Nature publishing group.

process to eliminate most of the functional groups. One representative method is the exposure of graphene oxide to hydrazine, hydrides, hydroquinone and p-phenylene diamine. Thermal reduction at over 200°C is another method to decompose graphene oxide.<sup>20</sup>

On the other hand, CVD graphene can be synthesized on a metal catalyst such as Ni and Cu.<sup>23–25</sup> The properties of the resulting graphene films strongly depend on the growth mechanism relying on the catalyst layer used. Figure 1(b) illustrates the growth mechanism of graphene films by a CVD process for metal catalyst layers. For a Ni catalyst layer, the hydrocarbon atoms diffuse into Ni at a temperature of around 1000°C. In the cooling process, graphene films grow on Ni when an appropriate cooling rate is adopted.<sup>24</sup> Because of the thermal expansion difference between the graphene film and the Ni catalyst, wrinkles and a rough surface morphology are observed [see Fig. 1(c)]. The synthesized graphene film has various layers owing to a certain amount of solubility with Ni. In addition, the mechanism of graphene growth on Cu is based on an adsorption phenomenon caused by the extremely low solubility of the carbon atoms.<sup>27–29</sup> Adsorbed carbon atoms form seeds, from which graphene growth starts at 1000°C. Graphene films grown on Cu catalyst show monolayer coverage over 90%.<sup>25</sup> Synthesis of graphene films on Cu results in wrinkles as well as steps due to thermal expansion differences. Graphene films grown by CVD can be transferred onto an arbitrary substrate by several different methods, which will be discussed later.

# 2.2. Transparent conductive graphene film formation

Synthesized rGO and CVD graphene need to be formed on arbitrary substrates in order to utilize them for transparent conductive films.<sup>18,21</sup> Figure 2 illustrates the process of fabricating rGO transparent conductive films. Graphene oxide is dispersed in solution by Hummer's method, which is discussed in the synthesis section, as the starting point of fabricating rGO thin films. Once a graphene oxide solution is produced, graphene oxide films can be formed on arbitrary substrates by drop-casting, dipcoating, spraying, spin-coating, electrophoresis,



Fig. 2. Process diagram of fabricating rGO-based transparent conductive films.

Langmuir–Blodgett (L–B)/Langmuir–Schaefer or transfer via vacuum filtration.<sup>21,30</sup>

Among these, the spin-coating and L–B methods can provide uniform and continuous conductive films on arbitrary substrates. Spin-coating of graphene oxide requires high concentrations  $(0.5-3 \,\mathrm{mm/mL})$ to produce a uniform and continuous film. The thickness of the graphene oxide can be determined by the density of the graphene oxide and the number of spin-coating processes.<sup>21</sup> In the L–B method, graphene oxide flakes are floated on a water/air interface and methanol or isopropanol is slowly added to the graphene oxide solution.<sup>30</sup> When the electro-repulsive force between the carboxyl functional groups on the edges of the graphene oxide flakes overcomes the electro-attractive force between the functional groups on the graphene oxide surface, the monolayer is floated at the water and air interface. These flakes can then be deposited on substrates by lifting them from solution. The thickness of a graphene oxide film can be controlled by the number of repeated processes. rGO transparent conductive films are produced by hydrazine exposure or thermal annealing of the graphene oxide film.<sup>26,29</sup>

In regards to CVD graphene films on catalysts, many researchers have focused on effective transfer methods onto arbitrary substrates. Figure 3 shows the transfer procedure and an image of graphene films on a transparent substrate. In order to utilize CVD graphene films as a transparent conductive layer, they must be separated from the metal catalyst. In this step, graphene films should be protected from high stress, which can result in cracks and defects.<sup>14,26,27</sup> Figure 3(a) shows roll-to-roll-based transfer process assisted by thermal release tape (TRT) support.<sup>14</sup> Once the graphene film/Cu foil is attached to the TRT in the first lamination process, the Cu foil can be etched using an etchant solution such as ammonium persulfate or FeCl<sub>3</sub> in a second roll process after removing the backside graphene by oxygen plasma treatment. The TRT/graphene is then attached to a target substrate by the attractive force of TRT. Finally, the graphene film is transferred by heating in a third lamination process, which eliminates the attractive force of TRT. Repeated cycles of this treatment result in thicker graphene transparent conductive films, with thickness being proportional to the number of cycles. Figures 3(b) and 3(c) show images of CVD graphene on transparent and flexible PET substrates transferred by these process.

In addition, in case of graphene growth on wafer coated with metal catalysts, polymer support made of a material such as Poly(methylmethacrylate) (PMMA), (Polydimethyl-siloxane) (PDMS) or TRT is attached to the surface of the graphene film. The polymer supports/graphene film/metal layers are spontaneously detached from the SiO<sub>2</sub>/Si wafer when exposed to water because of the wettability difference between metal and SiO<sub>2</sub>.<sup>26</sup> Gentle sonication is able to assist this process. The bottom metal catalyst can then be removed by etchants such as FeCl<sub>3</sub> or FeNO<sub>3</sub>. The graphene film can then be transferred onto an arbitrary substrate by removing the polymer supports.

# 2.3. Properties of transparent conductive graphene films

Raman spectroscopy and optical transmittance measurement are commonly used to estimate the crystalline quality and thickness of graphene films.<sup>4,31-33</sup> Figure 4 shows the results of Raman spectroscopy and optical transmittance spectroscopy analysis of rGO and CVD graphene films. In Raman spectroscopy of graphene, there are several significant peaks: D, G and 2D, which are



Fig. 3. Schematic illustration of CVD graphene-based transparent conductive films. (a) Roll-to-roll transfer process of graphene film grown on Cu foil. (b) and (c) Flexible and transparent conductive film-based graphene film from Ni and Cu catalyst. Reproduced with permission from 26. Copyright (2010), American Chemical Society.

located at  $1350 \text{ cm}^{-1}$ ,  $1580 \text{ cm}^{-1}$  and  $2680 \text{ cm}^{-1}$ , respectively.<sup>31–33</sup> The red line in Fig. 4(a) shows the Raman spectra of exfoliated graphene on a SiO<sub>2</sub> substrate, which shows almost perfect crystalline sp<sup>2</sup>-bonded carbon atoms. Here, the G peak indicates the electronic resonation with the injected laser, revealing the electronic states in the graphene lattice. The 2D peak is related to lattice phonons, as estimated by the double resonance of the excited electrons of K-K' states. The G/2D ratio and the splits of the 2D peak can allow for the determination of the number of layers of graphene. The ratio between the D and G peaks is an indicator of defects and disorder in the graphene lattice.

Raman spectroscopy of graphene oxide and rGO films, shown in black and blue in Fig. 4(a), respectively, can reveal the presence of crystalline defects and disorder by a high D/G ratio. The sp<sup>2</sup> ring cluster size can be determined by the area ratio between the D band and G band. The Raman spectra of CVD graphene film shows similar results to that of exfoliated graphene [see Fig. 4(b)]. According to Raman spectrum of graphene grown on Cu, it mostly shows monolayer of graphene

with low lattice disorder, indicated by the negligible intensity of the D peak.<sup>14</sup> As the number of graphene layers increases with repeated transfer process, the shape of the Raman spectrum is preserved, while the peak position is shifted in the 2D and G peaks due to the doping effect.

The thickness of graphene film is inversely proportional to its transmittance [see Figs. 4(c) and 4(d)]. An repetitive fabrication steps of rGO films and CVD graphene films on substrates result in thicker graphene films, as indicated by a decreased transmittance value.<sup>14,34</sup> The sheet resistances of graphene films are also related to the film thickness.

As shown in Fig. 5(a), the sheet resistance value of a rGO film decreases from  $10^{11}$  to  $10^5 \Omega/\text{sq}$  as the transmittance decreases from 97 to 60%. In the case of CVD graphene from Cu, the sheet resistance values decreases from 300 to  $50 \Omega/\text{sq}$  as the number of layers increases from 1 to 4. Nitric acid or gold chloride doping can additionally reduce the sheet resistance of CVD graphene films by ion adsorption, yielding  $30 \Omega/\text{sq}$  for four-layered graphene, which is superior to conventional transparent electrodes such as ITO or CNT films [see Fig. 5(b)].<sup>14</sup> Furthermore,



Fig. 4. Optical analysis of rGO and CVD graphene. (a) Raman spectra of GO and rGO comparing with that of pristine graphene. Reproduced with permission from 19. Copyright (2008), American Chemical Society. (b) Raman spectra of CVD graphene film with respect to number of layers by repetition of transfer process. (c) and (d) Optical transmittance of rGO films and CVD graphene films according to their thickness. Reproduced with permission from 34. Copyright (© 2008, American Institute of Physics (color online).



Fig. 5. Sheet resistance of graphene films according to various thickness indicated by transmittance. (a) Sheet resistance of transparent conductive film based on rGO. Reproduced with permission from 18. Copyright © 2008, American Institute of Physics and (b) Sheet resistances of CVD graphene film compare with various transparent conductive films. Reproduced with permission from 14. Copyright (2010), Nature publishing group.

graphene films have better flexibility than ITO. When a external strain is applied to graphene films and ITO, the relative resistance value of the graphene is preserved, while that of ITO is drastically increased due to the formation of micro-cracks.<sup>14</sup> For these reasons, many researchers have investigated the possibility of utilizing graphene in flexible transparent conductive films.

### 3. Applications of Transparent Conductive Graphene Films

#### **3.1.** Touch screens

One potential application of transparent conductive films is touch screens, which have been adopted in various electronic devices such as cell phones and e-books. There are several types of commercialized touch screens in the market. Resistive-type touch screens are operated through induction of an electric short between top and bottom transparent conducting films. They require a resistance of up to  $550 \,\Omega/\mathrm{sq}$  and an optical transmittance of over 90%at a 550 nm wavelength. Typically, ITO films have been widely used in this application. CVD graphene films can meet this 550 nm requirement and also be formed on arbitrary substrates. Figure 6 shows a graphene-film-based resistive-type touch screen formed on flexible PET substrates.<sup>14</sup> In graphene/ PET films, the active area is defined through lithography or oxygen plasma treatment with the use of a shadow mask. After the formation of the contact electrode and the signal transport line by screen printing with silver paste, the x- and y-axis are defined at the top and bottom, respectively [see Fig. 6(a)]. The top and bottom films are assembled

together by adhesive tape with a spacer at bottom of the graphene to prevent spontaneous electrical short. A fabricated flexible graphene-based touch screen is shown in Fig. 6(b). Since all of the materials are flexible, the screen shows reliable operation after many bending cycles.

In addition, capacitive touch screens fabricated using transparent graphene films are also available, since graphene films can satisfy the requirement of a sheet resistance value of under 100  $\Omega/sq$  through doping. We expect that transparent graphene films would replace rigid and brittle ITO films in touch panel screen electrodes.

#### 3.2. Organic light-emitting diodes

An important component of OLEDs is the anode, which inject charge carriers and allow light to pass through. ITO, which is a representative transparent electrode material, has several drawbacks as mentioned above. In particular, ITO over 100 nm in thickness shows fracture strain less than 1%, which is a serious obstacle for developing flexible OLEDs.<sup>35</sup>

Graphene films are attractive materials for transparent conductive electrodes in OLEDs due to their controllable transparency, good electrical conductivity and tunable work function. Many researchers have investigated the use of graphene films as transparent electrodes for the purposes of both replacing ITO and also developing flexible OLEDs. In particular, graphene films have a molecular structure similar to that of organic electronic materials, and thus can form strong bonds with organic electronic materials.<sup>36–39</sup>



Fig. 6. (a) Structure of graphene-based resistive-type touch screen and (b) Image of flexible touch screen-based on graphene films. Reproduced with permission from 14. Copyright (2010), Nature publishing group.

Figure 7 shows the structures and performances of rGO- and CVD-graphene-based OLEDs. In these back emission OLED structures, graphene films were used as anodes in place of ITO, as the work function of graphene films has been reported to be in the range of 4.3 to  $4.4 \,\mathrm{eV}$ , which corresponds closely to the work function energy range of OLED anodes.<sup>36,37</sup> OLEDs based on a rGO electrode, as shown in Fig. 7(a), used a rGO or ITO anode/poly (3.4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS)/N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl-4,4'-diamine(NPD) (50 nm)/tris (8-hydroxyquinoline) aluminum (Alq3)(50 nm)/lithium fluoride (LiF) (0.3 nm)/Al cathode structure on quartz substrates for bottom emission.<sup>36</sup>

Figure 7(a) shows the current density and luminescence characteristics with respect to applied bias for both rGO-based and ITO-based devices. These

rGO-based and ITO-based devices are turned on at a voltage of 4.5 and 3.8 V, and show  $10^2$  and  $10^3$  $mA/cm^3$  current density levels at 15 V, respectively. Because of the high resistance of rGO electrodes  $(\sim 800 \,\Omega/\text{sq})$  compared with that of ITO  $(\sim 20 \,\Omega/$ sq), the voltage drop in the rGO electrode becomes dominant, which results in a lower current density at high applied voltage levels. Likewise, the luminescence difference between the two devices was on an order of magnitude at 15 V, for a reason similar to that of the differences in current density and optical out-coupling. Figure 7(b) shows the EQE and LPE of both devices with respect to current density. Even though the sheet resistances and hole injection barriers of rGO electrodes are much higher than those of ITO electrodes, the EQE and LPE of the two devices are comparable in value. This may be because of the strong bonding with organic materials, which can



Fig. 7. Performance of graphene film-based OLEDs. (a) Current density and luminance versus applied voltage for rGO film and ITO-based OLEDs. (b) External quantum efficiency (EQE) and Luminous power efficiency (LPE) of OLEDs made up with ITO and rGO film. Reproduced with permission from 36. Copyright (2010), American Chemical Society. (c) and (d) Luminance and luminous efficiency versus applied voltage for different CVD graphene layers and doping methods. Reproduced with permission from 37. Copyright (2012), Nature publishing group.

NANO 2013.08. Downloaded from www.worldscientific.com by YONSEI UNIVERSITY on 06/21/13. For personal use only. improve the hole injection efficiency.

Many OLEDs based on CVD graphene films have been reported.<sup>38–40</sup> Among them, OLED devices based on graphene films from copper foils show extremely high performance compared with those based on ITO.<sup>37</sup> Graphene films transferred onto PET substrates have been used as an anode material that can be controlled in terms of electrical resistance, optical transmittance and work function by random piling of multiple layers and acid doping [see Figs. 7(c) and 7(d)]. The sheet resistance and work function varied from 189 to 89 Ohm/sq and 4.33 to 4.45 eV as a function of the number of layers, which varied from 2 to 4 layers. The optical transmittance decreases by 2.3% when graphene layers are piled up. Nitric acid treatment can result in ion adsorption onto the graphene film surface, which changes the sheet resistance and work function. In particular, the sheet resistance and work function of four-layered graphene changed to  $50 \Omega/sq$  and 4.62 eV, respectively after nitric acid treatment for 20 seconds. GraHIL composed of PEDOT:PSS and PFI results in a work function gradient from the anode to the NPB, so that the hole carrier can be easily transported through this layer despite the presence of a large hole injection barrier ( $\sim 1.0 \,\mathrm{eV}$ ). The devices were turned on at an applied voltage of around 2V and showed different luminances with respect to anode material. This difference is closely related to the conductance and hole injection efficiencies of anode materials. The luminance of devices incorporating graphene films is proportional to the number of graphene layers, and the current

density and work function of graphene film anodes can thus be tuned. Devices using graphene films anodes doped with gold chloride  $(AuCl_3)$  show higher luminance, which can be attributed to a higher conductance  $(30 \,\Omega/sq)$  and work function  $(5.0 \,\mathrm{eV})$ . Figure 7(d) shows the luminous efficiency of OLED devices with various electrodes. The luminous efficiency is increased as a function of the number of graphene layers. In particular, the device employing a four-layered graphene anode doped with nitric acid shows the highest luminous efficiency of  $37.2 \,\mathrm{lm/W}$ , while the device containing an ITO anode shows a luminous efficiency of 24.1 lm/W. Indium atoms diffused into the interface between ITO and the organic materials after fabrication could act as trap centers for injected hole carriers, which degrades the hole injection efficiency of OLED devices. In contrast, diffusion of conducting atoms into the interface of graphene film anodes is not possible, and devices made with graphene film anodes show higher luminous efficiency. Though graphene anodes doped with gold chloride show a higher conductivity and work function than those doped with nitric acid, the maximum luminous efficiency is  $28.1 \,\mathrm{lm/W}$  since gold nanoparticles on the graphene film can lead to leakage current in the device.<sup>37</sup>

Graphene films show a homogeneous optical transmittance distribution in the visible range, while ITO shows a slanted transmittance distribution in the blue range [see Fig. 8(a)]. Four-layered graphene exhibits over 90% optical transmittance at 550 nm. Organic light-emitting diodes incorporating graphene



Fig. 8. Transparency and flexibility of OLED devices. Reproduced with permission from 38. Copyright (2012), Nature publishing group. (a) Comparison of doped graphene films with other transparent conducting electrode such as CNT and ITO and (b) Bending stability of graphene film estimated by current change along with the number of bending cycles.

film anodes can thus emit homogeneous visible light with luminance intensity comparable to ITO and a higher luminous efficiency. In addition, graphene film anodes allow for mechanical flexibility in OLEDs since graphene films can endure a tensile strain over 7%. Figure 8(b) shows the results of bending cycle tests of OLED devices made with either graphene film or ITO anodes. Both devices were subjected to a bending strain of 1.25% for 1000 cycles. The graphene-anodebased OLED device shows excellent bending stability, while the ITO-based OLED device broke at 800 cycles.

#### 3.3. Organic photovoltaic cells

Many researchers have worked on applying graphene films as counter electrodes for transparent electrodes for OPVs.<sup>40-44</sup> OPVs require a counter electrode to achieve efficient carrier transport and thus a high charge collection efficiency.<sup>40-44</sup> In order to achieve this goal, graphene films with low electrical resistance and high work function must be developed. The sheet resistance and work function of graphene can be tuned by the number of layers and doping, in order to produce high-efficient OPV.

Figure 9 shows the structure and characteristics of OPV cells made with rGO and CVD graphene film as counter electrodes.<sup>41</sup> The cell is composed of a rGO electrode/PEDOT:PSS for the hole transport layer and an electron blocking layer/P3HT:PCBMbased bulk heterojunction  $((BHJ)/TiO_2$  nanoparticles/Al electrode. An energy diagram of the cell is shown in Fig. 9(a). With OPV cells containing rGO electrodes, the thickness of the rGO is one of the important factor in order to achieve maximum power conversion efficiency (PCE). The performance of the device depends on the charge collection efficiency of the P3HT:PCBM active layer. Therefore, the electrical conductivity and the optical transmittance of electrode are critical factors for high-efficient OPV. The electrical conductivity of the rGO film tends to increase, while the optical transmittance decreases as its thickness increases.<sup>14,35</sup> Accordingly, it is important to optimize the thickness of the rGO electrode for a high PCE.

Bulk heterojunction cells made with various rGO film thicknesses (4, 10, 16 and 21 nm) were fabricated in order to determine the optimal thickness.<sup>41</sup> In the J–V curves of four different cells shown in Fig. 9(b), a comparable open-circuit voltage ( $V_{\rm oc}$ ) of 0.56 V was observed, which was driven by the energetic

relationship between the donor and acceptor in the P3HT:PCBM-based BHJ structure. The fill factor (FF) is varied slightly from 30 to 32% as a function of rGO film thickness, which can be attributed to decreased sheet resistance. The short circuit current density  $(J_{sc})$  of the devices increased from  $1.74 \,\mathrm{mA}/$  $\rm cm^2$  to  $4.39 \,\rm mA/cm^2$ , which results in enhancement of the PCE from 0.28 to 0.78%. Nevertheless, further increase in the thicknesses of rGO films result in degradation of PCE due to a decreased  $J_{sc}$  by the optical out-coupling effect. It is believed that the sheet resistance of a rGO film determines the hole collecting efficiency from the HOMO level of the P3HT:PCBM active layer up until a certain thickness, at which point the system becomes sensitive to the optical out-coupling effect.<sup>40,41</sup>

On the other hand, OPV cells composed of CVD graphene films show a higher PCE, which can be attributed to a higher optical transmittance and conductance.<sup>42-44</sup> It is widely understood that the sheet resistance and work function of a CVD graphene film can be engineered by random stacking or doping.<sup>14,43</sup> For this reason, many researchers have attempted to fabricate OPV cells with CVD graphene films.<sup>43</sup> A representative report is illustrated in Figs. 9(c) and 9(d). The structure of this cell is basically the same as that of the cell in Fig. 9(a). In particular, a interfacial thin layer of  $MoO_3$  between the CVD graphene electrode and the PEDOT:PSS hole transport layer was adopted. The role of this additional thin layer is to increase the work function of the CVD graphene film from 4.3 to 5.47 eV. Separate hole carriers in the active layer can easily transport to a graphene charge collector since the increased work function of the graphene film reduces the energy barrier at the interface between the graphene film and the PEDOT:PSS layer. Another benefit of the  $MoO_3$  thin layer is improvement in the hydrophilicity of the graphene film, as it provides a smooth surface over the PEDOT:PSS layer. The J–V curves of OPV cells show a PCE change with respect to the different number of graphene electrodes. The cell consisting of four-layered graphene shows the best photovoltaic performance, with a PCE value of 2.5%. This value is very close to the PCE value of ITO devices. The reason for this higher PCE value is that the series resistance of four-layered graphene devices is lower than that of three- and five-layered graphene devices. Further improvement of the PCE of graphene devices can be achieved by either conductance enhancement of



Fig. 9. Structure and performance of OPV cells made up with graphene electrodes. (a) Energy diagram of bulk heterojunction OPV cells consisted of rGO anode. (b) Current density versus voltage curve of OPV cells with respect to different thickness of rGO film. Reproduced with permission from 41. Copyright (2010), American Chemical Society. (c) Structure of OPV cells based on CVD graphene film as anode and (d) Current density versus voltage curve of OPV cells with respect to different number of graphene layers. Reproduced with permission from 43. Copyright (2011), WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

four-layered graphene via more effective doping or interface engineering to reduce series resistance. By optimizing these fabrication processes, graphene-based OPV cells could be commercialized. These cells can provide other advantages such as flexibility, chemical robustness and roll-to-roll processability.

#### 3.4. Thin film transistors

For future electronics, unusual form of devices has been demanded. For the sequences, organic-based semiconductors have been studied for several decades due to their own flexibility. However, metal electrode, which is used for a long time, is brittle, opaque and cannot make good contact with organic-based semiconductors because its thickness break the continuous step coverage between electrode and channel material. Graphene films, an atomically thin electrode, synthesized by the CVD method, would be a good answer for the problem because it provides good continuity of alignment of channel material over electrodes.<sup>45-47</sup>

A bottom gate structure, which is a general structure for polymer-based transistor, is shown in the inset of Fig. 10(a).<sup>47</sup> The current-voltage



Fig. 10. Pentacene TFTs based on source and drain graphene electrode. Reproduced with permission from 47. Copyright (2011), WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (a) Output characteristic of flexible penetacene TFTs consisted of graphene electrodes. (b) Contact resistance between pentacene and different source/drain electrode materials. (c) Comparison of charge carrier mobility between two devices based on graphene film and Au electrodes and (d) Transfer characteristic of pentacene TFTs with respect to different sequential process.

characteristic shows the ohmic contact, between graphene and semiconductor layer as shown in Fig. 10(a). Figure 10(b) shows the width normalized contact resistance as a function of gate voltage of the devices with gold electrode and graphene electrode. The normalized contact resistance of the device with graphene electrode shows more than 100 times lower than that of the device with gold electrodes. This phenomenon strongly depends on the continuity of the alignment of the pentacene. Due to the small contact resistance, average mobility of the device with graphene electrodes is 100 times higher than that of the device with gold electrode as shown in Fig. 10(c).

Interestingly, the electrical property of the device strongly depends on the process sequence as shown in Fig. 10(d); P-T process means that patterning

process of the graphene has been done before transfer process while T-P process that transfer process has been done before patterning process. The main difference between two process is the roughness of the surface between semiconductor layer and dielectric layer. The surface of dielectric layer can be damaged by O<sub>2</sub> plasma, which is used for patterning process of graphene. This difference makes difference in alignment of the pentacene, which results in different electrical property of the device. (T-P process:  $0.01 \text{ cm}^2/\text{Vs}$ , P-T process:  $0.12 \text{ cm}^2/\text{Vs}$ ).

Recently, graphene has been utilized as the electrodes of CNT transistors due to the low contact resistance between them. It is expected that graphene films interact with CNTs through  $\pi-\pi$  attractive interaction.<sup>48</sup> Figure 11(a) shows flexible CNT device made of a CNT channel, a Su-8 gate dielectric and



Fig. 11. CNT transistor with CVD graphene electrodes. Reproduced with permission from 48. Copyright (2010), IOPscience. (a) Structure of all carbon-based flexible transistor. (b) SEM image of contact region between CNT and graphene electrodes. (c) and (d) Output and transfer characteristic of CNT transistor with graphene film electrodes. (e) Contact resistance between CNT channel and graphene electrode and (f) mobility stability of all carbon-based transistor as a function on bending strain.

graphene film as electrodes. The SEM image of Fig. 11(b) exhibits that the atomically thin graphene film allows continuous step coverage at the boundary between the electrode and the CNT channel. The output and transfer characteristics of the device shown in Figs. 11(c) and 11(d), respectively, indicate typical p-type behavior of CNT device with Ohmic contact. This device has an effective mobility of  $2 \text{ cm}^2/\text{Vs}$ , an on/off ratio of  $10^2$ , and a threshold voltage of around -7 V. The contact property between the CNT channel and the graphene is investigated by the transmission line model (TLM) as shown in Fig. 11(e). The transmitted lines in the figure intersect at zero, meaning that the interface

has negligible contact resistance due to intimate contact between the materials. In addition, the performance of this device is retained during the 2% of tensile and compressive strain levels [see Fig. 11(f)].

In addition, graphene can be utilized as semiconductor channel as well as S/D electrodes and form TFT with a monolithic device structure.<sup>49</sup> Since graphene films have applications in high-performance transistors in terms of charge carrier mobility,<sup>1-3</sup> it is expected that they can be simultaneously utilized for semiconducting channel materials and contact electrodes. A stretchable, high-performance graphene transistor with a monolithic structure, composed of channel and electrodes with various number of graphene layer, and dielectric layer consist of poly (styrenemethyl methacrylatestyrene) (PSPMMA-PS) triblock copolymer and 1-ethyl-3-methylimidazolium bis (trifluoromethyl- sulfonyl)imide ([EMIM] [TFSI]) ionic liquid was fabricated as shown in Fig. 12(a).

Since a high capacitance value of ion gel  $(5.1 \,\mu\text{F}/\text{cm}^2 \text{ at } 10 \,\text{Hz})$  due to electric double layer at both interfaces between the graphene/ion gel and the gate electrode/ion gel, fabricated devices were operated within a low gate voltage of 2 V, and represent high on current. As the number of layers are increased up to 3 layers, the corresponding hole and electron mobility changes proportionally from 26 and 20 cm<sup>2</sup>/



Fig. 12. Monolithic transistor based on CVD graphene layers. Reproduced with permission from 50. Copyright (2010), American Chemical Society. (a) Structure of monolithic transistor consisted of graphene films. (b) Electron and hole mobility of monolithic transistor as a function of different number of graphene layers. (c) Transfer characteristic of monolithic transistor consisted of graphene films. (d) Stability of charge carrier mobility and drain current with respect to stretching strain up to 5% and 3% stretching cycles.

Vs to 1131 and  $362 \text{ cm}^2/\text{Vs}$ , respectively [Figs. 12(b) and 12(c)]. The poor electrical property of monolayer graphene is presumed that the charge scattering caused by moisture or other chemical residue at the porous structure of the PDMS and it can be overcomed by multiple stacking methods. Due to the weak interlayer coupling between each graphene layers, the charge scattering is efficiently screened via stacked graphene layer. Thus, the graphene transistors with stacked graphene show remarkable increases in charge carrier mobility. Moreover, the materials in this device are optically transparent and mechanically stretchable. The performance of the device was stable up to a 5% strain due to the high mechanical strength of the materials [see Fig. 12(d)]. In addition, the device shows performance independent of fatigue up to a 3% strain level.

Therefore, it is believed that graphene electrodes make conformable contacts with carbon-based semiconducting materials such as pentacene, P3HT, CNT and graphene. The resulting graphene electrode devices showed even higher performance compared with conventional metal electrodes.<sup>45–49</sup> In addition, fabrication of devices with graphene electrodes is simpler because transfer printing of ultrathin graphene films can be performed under low temperatures and ambient pressure. For this reason, graphene films can be used as a primary electrode material for carbon-based transistor devices.

#### 4. Conclusion

Graphene has shown great potential in the field of transparent conductive electrodes. Large-area graphene synthesis methods can be realized by both top-down and bottom-up approaches, i.e., rGO and CVD. The resistance or the work function of graphene films can be tuned for various applications. Many applications such as touch screens, OLEDs, OPVs and TFTs employing graphene show comparable or outstanding performance with respect to conventional devices. In addition to such electrical applications, graphene films would be useful for fabricating physical<sup>50</sup> and chemical sensors<sup>51,52</sup> and energy storage and harvesting devices.<sup>53</sup> Thus, we believe that graphene would provide a great opportunity for the development of high performance electronic devices.

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