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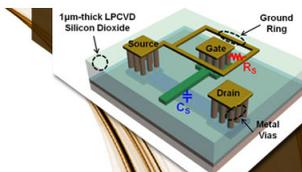
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Transparent conductive thin films of single-wall carbon nanotubes encapsulating dopant molecules

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Transparent conductive thin films of single-wall carbon nanotubes (SWCNTs) doped with organic dopant molecules encapsulated inside the SWCNTs are reported. Doping with tetrafluorotetracyano-*p*-quinodimethane encapsulated within the SWCNTs improved the ratio of direct current to optical conductivity in the SWCNT thin films by a factor of about 1.8. Thermal stability of the improvement in electrical conductivity by encapsulation doping is investigated as a function of annealing temperature. We found that encapsulation doping provides stable conductivity enhancement in transparent thin films of SWCNTs compared to doping by adsorbed dopant molecules outside the SWCNTs. © 2012 American Institute of Physics. [doi:10.1063/1.3684811]

Transparent conductive thin films are widely used as electrodes in organic electronic devices. Such films are typically made from doped metal oxides such as indium tin oxide.¹ However, due to rising material cost and the brittleness of metal oxides, new materials for transparent conducting films are urgently desired. Thin films of single-wall carbon nanotubes (SWCNTs) have attracted much attention in recent years as an alternative to metal oxide electrodes.^{2–5} Transparent conductive films of SWCNTs provide high flexibility and ease of processing at low temperatures. Several groups have demonstrated flexible plastic devices such as organic light emitting diodes^{6,7} and photovoltaic devices^{8,9} that use transparent electrodes made from SWCNT films.

Chemical doping is a promising technique to improve electrical conductivity of SWCNT films. The conductivity of SWCNT films can be increased by doping with adsorbed dopant molecules such as acids^{4,5} and organic molecules¹⁰ on the walls of SWCNT. Geng *et al.* reported that HNO₃ treatment reduced the sheet resistance of transparent conductive films by a factor of 2.5.⁴ In addition to improving electric conductivity, durability of carrier doping is also required to employ doped SWCNT films for practical applications. Several groups have reported stable doping of SWCNT films by modification of the doping process¹⁰ and coating a passivating layer on the SWCNT films.⁵ Jackson *et al.* reported that improvement in electrical conductivity was stabilized by coating a thin layer of conducting polymer on SWCNTs films doped with SOCl₂ and HNO₃.⁵ However, further studies on improvements in durability of doping are required for practical uses of transparent conductive thin films with doped SWCNTs.

Introducing fullerenes^{11,12} and other organic molecules¹³ into the inner spaces of SWCNTs alters their electronic and conducting properties. In one study, the p-type field effect transistor behavior of SWCNTs was changed to be ambipolar

by the insertion of fullerenes into SWCNTs.¹⁴ Carrier doping of SWCNTs was achieved by encapsulating dopant organic molecules.¹³ Doping by encapsulation results in improved stability of doping states in air as compared with that by adsorbed molecules, because the dopant molecules are protected from ambient air by the wall of the SWCNTs.

In this study, we have demonstrated transparent conductive thin films using SWCNTs doped with organic dopant molecules encapsulated within. Doping by encapsulated dopant molecules is expected to yield stable conductivity enhancement in transparent conducting thin films of SWCNTs. We investigated the thermal stability of the improvement in electrical conductivity by encapsulation doping.

The encapsulation of dopant molecules into SWCNTs was achieved by a gas phase method.¹² Tetrafluorotetracyano-*p*-quinodimethane (F₄TCNQ) was used as the dopant molecule in this work. SWCNTs with an average diameter of 1.9 nm, synthesized by the enhanced direct injection pyrolytic synthesis (eDIPS) method,¹⁵ were oxidized at 600 °C for 30 min in air. The treated SWCNTs and F₄TCNQ molecules were vacuumed at 2×10^{-4} Pa and heated at 100 °C for 1 day. The obtained samples were heated using a heat gun to remove F₄TCNQ adsorbed on the surface of the treated SWCNTs. A control SWCNT sample was also fabricated via the above procedure without F₄TCNQ. Thin films of F₄TCNQ encapsulated SWCNTs and control SWCNTs were prepared by spraying their 1,2-dichlorobenzene dispersion on glass substrates using an airbrush. Sheet resistance of the thin films was measured by the four-point probe technique at room temperature. Transmittance characteristics and surface morphologies of the films were characterized by a spectrophotometer (JASCO V-570) and a scanning electron microscope (SEM, Hitachi S-3000 H), respectively. X-ray diffraction (XRD) was carried out using a Rigaku x-ray diffractometer with a Cu-K α x-ray source at a total power of 1.2 kW. Raman measurements were performed using a Raman spectrometer (JASCO NRS-1500 W) at room temperature. The excitation line used for the Raman measurement was 532 nm.

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XRD measurements were carried out to confirm the encapsulation of dopant molecules into the SWCNTs. Fig. 1(a) shows XRD patterns of the F₄TCNQ doped SWCNTs and the control SWCNTs. A distinct peak around 4° corresponding to the (10) peak of the SWCNTs bundle structure was observed in the control SWCNT sample. On the other hand, the (10) peak almost disappeared in the doped SWCNT sample. It is well known that the intensity of the (10) peak is sensitive to molecular encapsulation into the SWCNTs.¹⁶ Therefore, such behavior provides evidence for encapsulation of F₄TCNQ molecules inside the SWCNTs.

The phenomenon of carrier doping by encapsulated F₄TCNQ molecules was confirmed by the Raman measurements. Fig. 1(b) shows the Raman spectra in the G-band region of the F₄TCNQ encapsulated SWCNTs and the control SWCNTs. The doping behavior can be characterized by the shift in the peak of the G-band. It is seen that the peak position of the G-band shifted from 1594 cm⁻¹ to 1605 cm⁻¹ by encapsulation of the F₄TCNQ molecules. This change is consistent with a previous report of hole doping.¹⁷

Fig. 2 shows SEM images of the thin films of F₄TCNQ encapsulated SWCNTs and the control SWCNTs on glass

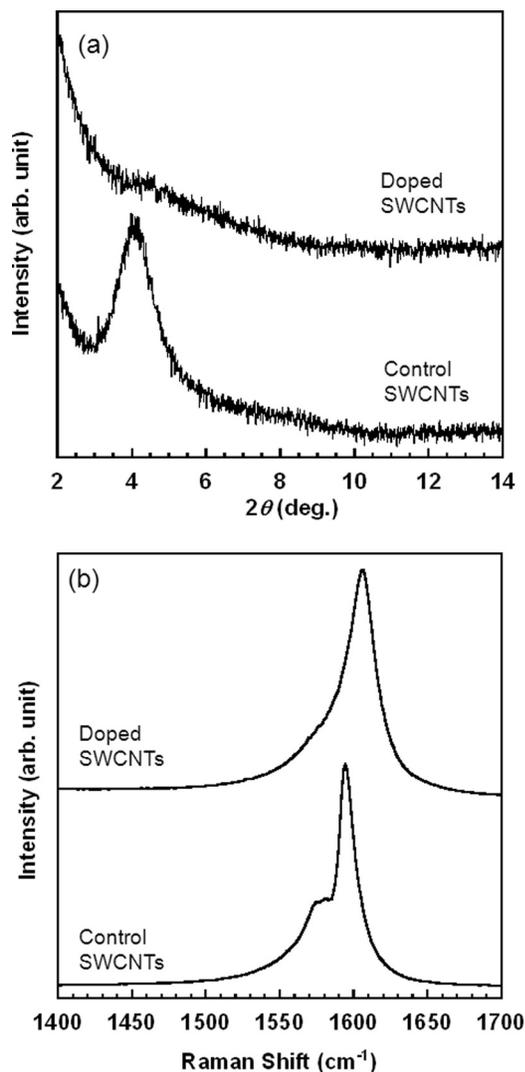


FIG. 1. (a) XRD pattern and (b) Raman spectra of the F₄TCNQ-doped and control SWCNT films. Intensity of Raman spectra is normalized at the peak intensity of the G-band.

substrates. Both samples show similar bundle size and network morphologies. Fig. 3 shows a plot of the transmittance versus sheet resistance of thin films of F₄TCNQ encapsulated SWCNTs and control SWCNTs. The thin films of doped SWCNTs show clear reduction in sheet resistance compared to the control SWCNTs with similar transparency. In contrast to the sheet resistance of 420 Ω/sq at 85% transmittance in the control SWCNTs films, the sheet resistance of the doped SWCNTs films was reduced to 220 Ω/sq at 84% transmittance. A commonly used figure of merit for transparent conductive thin films is the ratio of direct current conductivity (σ_{dc}) to optical conductivity (σ_{op}). σ_{dc}/σ_{op} can be estimated by curve fitting of a plot of the measured sheet resistance R_s versus transmittance T using the following equation:²

$$T = \left(1 + \frac{1}{2R_s} \sqrt{\frac{\mu_0}{\epsilon_0}} \frac{\sigma_{op}}{\sigma_{dc}} \right)^{-2}. \quad (1)$$

Here, μ_0 and ϵ_0 are the permeability and permittivity of free space, respectively. By fitting the data in Fig. 3 with Eq. (1), the ratio of σ_{dc}/σ_{op} was determined to be 5.5 and 9.9 for the control and doped SWCNTs films, respectively. Doping with F₄TCNQ encapsulation thus improved the ratio of σ_{dc}/σ_{op} by a factor of about 1.8.

We anticipated that stability of doping behavior is enhanced by the encapsulation of dopant molecules. To explore the durability of doping, the thermal stability of the electrical properties of a F₄TCNQ@SWCNT film was investigated by measuring the sheet resistance of the thin films after annealing at various temperatures for 20 min in air. We also characterized thin films of SWCNTs doped with

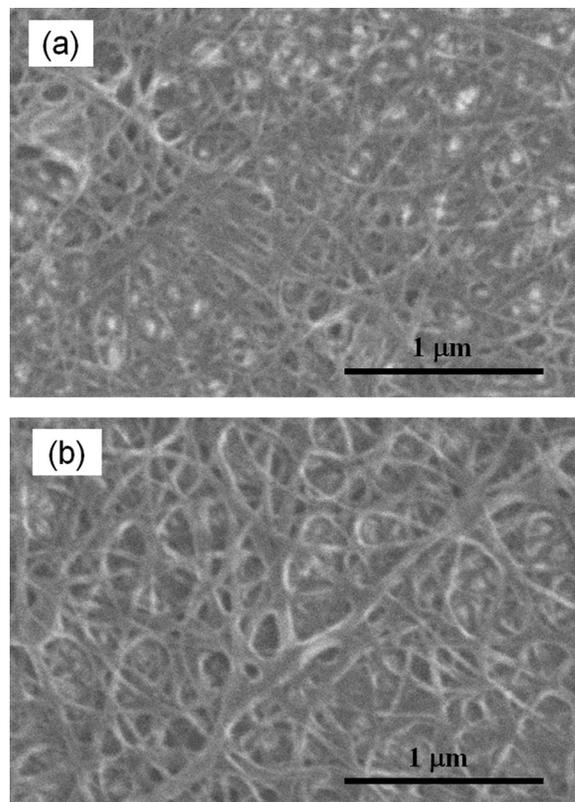


FIG. 2. SEM images of thin films of (a) SWCNTs encapsulating F₄TCNQ and (b) control SWCNTs.

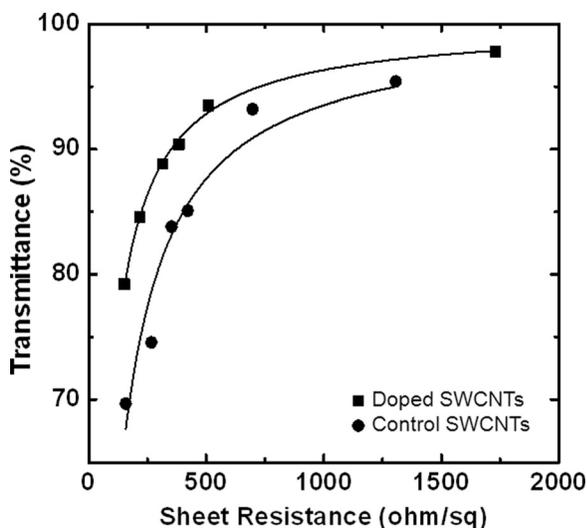


FIG. 3. Plot of the transmittance at 550nm versus sheet resistance of the thin films of F_4TCNQ encapsulated (squares) and the control (circles) SWCNTs. The solid lines indicate fitted curves using Eq. (1).

adsorbed dopant molecules on the sidewalls of the SWCNTs (Refs. 4, 5, and 10) in order to investigate stability enhancement by encapsulation doping. The SWCNT films doped with the adsorbed dopants were fabricated by dropping a F_4TCNQ -chloroform solution onto the SWCNT films. Fig. 4 shows a SEM image of the SWCNT film doped with adsorbed dopants. It is clearly observed that the SWCNT film is covered with F_4TCNQ . The SWCNTs film doped with the adsorbed dopant showed a sheet resistance of 160 Ω /sq at 85% transmittance. Fig. 5 shows the change in normalized sheet resistance of the thin films with 85% transmittance doped by encapsulated and adsorbed F_4TCNQ as a function of annealing temperature. The slight decrease in sheet resistance in both samples at around 100 $^{\circ}C$ may correspond to desorption of the solvent from the thin films. The SWCNTs film doped by adsorbed dopants shows a clear increment in the sheet resistance by annealing at more than 250 $^{\circ}C$. Doping by encapsulated F_4TCNQ molecules was thus seen to provide higher durability in electrical properties than that by adsorbed dopants. The thin films of encapsulation-doped SWCNTs maintained their sheet resistance at higher annealing temperature compared to those with adsorbed dopant.

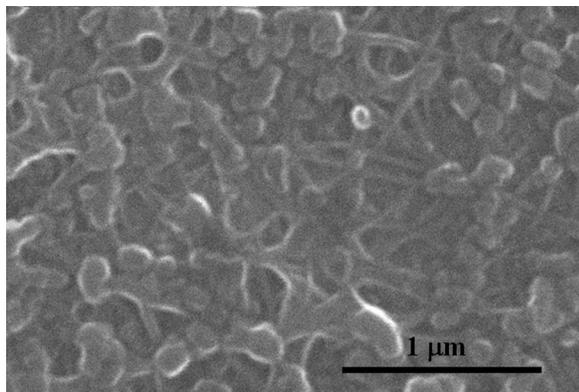


FIG. 4. SEM image of the SWCNTs film doped with adsorbed F_4TCNQ .

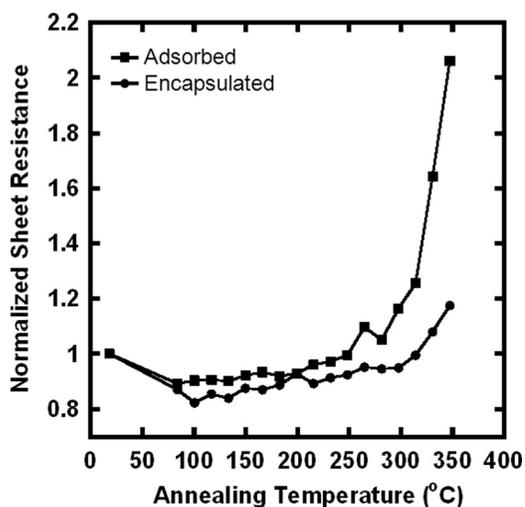


FIG. 5. Plot of the sheet resistance of the thin films with 85% transmittance as a function of annealing temperature. The sheet resistance is normalized to the value before the annealing process. Sheet resistance measurements were carried out at room temperature.

To confirm the relation between the change in sheet resistance and the doping condition, we measured Raman spectra after annealing at various temperatures. Fig. 6 shows

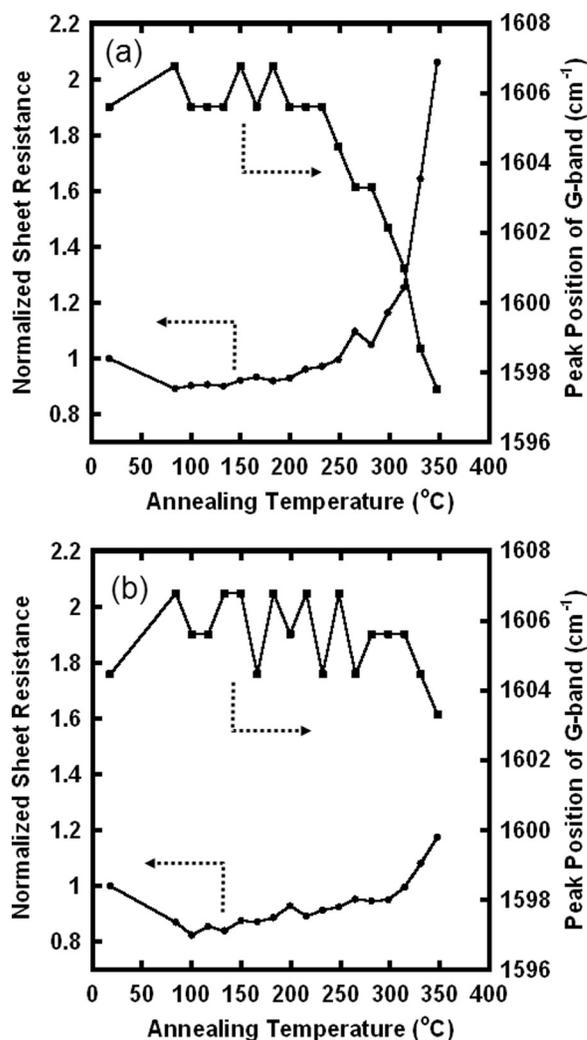


FIG. 6. Relationship between sheet resistance and peak position of the G-band of the SWCNT films doped with (a) adsorbed and (b) encapsulated F_4TCNQ molecules.

the relationship between the sheet resistance and peak position of the G-band of the SWCNT films doped by adsorbed and encapsulated F₄TCNQ molecules at various annealing temperatures. As shown in Fig. 6(a), the G-band peak position of the SWCNT film with adsorbed dopant is 1606 cm⁻¹ before annealing. The de-doping effect was observed with annealing at more than 250 °C by the downshifting of the peak position of the G-band. The peak position of the G-band was further shifted as the annealing temperature increased. The change in the sheet resistance was inversely proportional to the change in the G-band peak position, which indicates the doping condition. On the other hand, higher stability of doping behavior in the SWCNT film encapsulation doped with F₄TCNQ was confirmed by the dependence of the G-band peak position on the annealing temperature, as shown in Fig. 6(b). The slight de-doping in the F₄TCNQ@SWCNT film occurred with annealing at 350 °C as confirmed by the shift in the G-band peak to 1603 cm⁻¹. This phenomenon provides evidence for higher durability of doping behavior in the SWCNTs with encapsulation doping.

In summary, transparent conductive thin films were fabricated using F₄TCNQ@SWCNTs. Doping with F₄TCNQ encapsulation improved the ratio of direct current to optical conductivity in SWCNT thin films by a factor of about 1.8. Doping by encapsulated dopant molecules is expected to yield stable conductivity enhancement in transparent conducting thin films of SWCNTs. We found that encapsulation doping provides stable conductivity enhancement in transparent thin films of SWCNTs as compared to doping with adsorbed dopant molecules outside the SWCNTs.

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