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Integration of single-walled carbon nanotubes into polymer films by thermo-compression

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Abstract

We developed a simple and direct thermo-compression method for integrating single-walled carbon nanotube (SWCNT) mats of adjustable thicknesses, transparency and conductivity into polymer films. Produced SWCNT/polyethylene composite films have exhibited good optical transparency and conductivity as well as high mechanical flexibility. It was found that the electrical conductivity of the SWCNT mats could be significantly improved by ethanol densification. SWCNT/polyethylene thin films demonstrated excellent cold electron field emission properties.

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Keywords: Carbon nanotube; Conductive; Transparent; Flexible; Polymer; Field emission

Carbon nanotubes (CNTs) and especially single-walled CNTs (SWCNTs) are of great interest due to their unique and useful physical and chemical properties [1,2]. CNT based components have wide ranging applications including light-emitting diodes [3], transistors [4], filters [5], field emitters [6], photovoltaic devices [7] and fuel cells [8]. Ideally, even an individual CNT with a well defined property and in a specific location is sufficient for many applications [9]. However, to date, manipulation of individual CNTs is too difficult, time-consuming and expensive a task to be commercially viable [10–12]. Consequently, for many purposes thin films of CNTs with adjustable physical properties are preferable. Indeed, CNT film based devices have been already successfully used as gas detectors, transpar-
tion [20] have been proposed for transferring nanotubes onto plastics. Nanotubes can also be suspended in solution and sprayed [21] or spin coated onto, e.g., silicon wafers [22], however, such techniques require additional processing steps and equipment.

In this letter, we propose a simple thermo-compression method for easily and efficiently transferring SWCNT mats with adjustable thicknesses, transparency and conductivity into polymer substrates in a single-step process. The usefulness of this method is further demonstrated as a means of producing SWCNT/polyethylene (PE) field emission components.

In this work, SWCNTs were synthesized in a laminar flow aerosol (floating catalyst) reactor using carbon monoxide and ferrocene as a carbon source and a catalyst precursor, respectively [23]. SWCNT mats were then collected directly from the gas phase downstream of the reactor by filtering through 2.45 cm diameter nitrocellulose (or silver) disk filters (Millipore Corp., USA). The deposition temperature on the filter surface was also performed as well as laminating several layers of PE film, SWCNT mats were found to be successfully transferred.

Double sided lamination of SWCNT mats between PE films was also performed as well as laminating several layers of PE films with SWCNT mats in series. Fig. 2 presents transmission electron microscope (TEM) images of the sandwich structure of a 150 nm thick SWCNT mat laminated between PE films. For the TEM observation, a 50 nm thick cross-section of the film was prepared. The dark spots represent catalyst particles in the projection through the 50 nm layer. Low contrast between the CNTs and the PE substrate meant direct TEM observation of the individual tubes at low magnification was difficult, though higher magnification revealed evidence of their orientation. As one can see the mat structure appears uniform and homogeneous.

Since the as deposited CNT mats have low density and, as a result, low contact between tubes (Fig. 3a), prior to the measurements of the electrical properties, the mats of CNTs were

<table>
<thead>
<tr>
<th>Thermal treatment temperature (°C)</th>
<th>90</th>
<th>95</th>
<th>100</th>
<th>105</th>
<th>110</th>
<th>115</th>
<th>120</th>
<th>125</th>
<th>130</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmittance (%)</td>
<td>93.5</td>
<td>94.0</td>
<td>96.0</td>
<td>95.5</td>
<td>95.0</td>
<td>93.0</td>
<td>93.0</td>
<td>90.0</td>
<td>60.0</td>
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The optimal compression temperature from an optical transparence point of view was experimentally determined by heating films on a hot plate heated to different temperatures. Table 1 shows the transmittance (at a wavelength of 550 nm) of polymer films treated at various temperatures. The optical properties were measured with a Lambda 900 UV/vis/NIR spectrometer (Perkin-Elmer Life and Analytical Sciences, USA) after cooling the polymer film. PE films treated at 100 °C were found to be the most transparent.

For the integration of CNT mats into PE films, the following procedure was performed. The PE film was placed on a heating plate and heated to its thermal treatment temperature at a rate of 5–6 °C/min. Then the filter, coated with a SWCNT mat, was pressed against the heated PE film with a pressure of 0.35 N/cm² for 5–10 s. After removing the filter from the PE film, SWCNT mats were found to be successfully transferred. Fig. 2b presents a close-up of the transition region between the SWCNT mat, was pressed against the heated PE film with a pressure of 0.35 N/cm² for 5–10 s. After removing the filter from the PE film, SWCNT mats were found to be successfully transferred.

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Since the as deposited CNT mats have low density and, as a result, low contact between tubes (Fig. 3a), prior to the measurements of the electrical properties, the mats of CNTs were
Table 2
Effect of densifying SWCNT mats of different thicknesses with ethanol as measured by SEM (≥85 nm) and AFM (≤50 nm)

<table>
<thead>
<tr>
<th>Layer thickness before ethanol (nm)</th>
<th>24</th>
<th>35</th>
<th>50</th>
<th>85</th>
<th>100</th>
<th>1000</th>
<th>2930</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer thickness after ethanol (nm)</td>
<td>21</td>
<td>29</td>
<td>44</td>
<td>75</td>
<td>87</td>
<td>850</td>
<td>2600</td>
</tr>
<tr>
<td>Mat thickness decrease (%)</td>
<td>13</td>
<td>17</td>
<td>12</td>
<td>12</td>
<td>13</td>
<td>15</td>
<td>11</td>
</tr>
</tbody>
</table>

compacted by adding a droplet of ethanol to the transferred layer (Fig. 3b). Table 2 presents the increased densities (decreased layer thicknesses) of the studied nanotube mats as measured with SEM and AFM. In general, the densification of the SWCNT mats led to a change in thickness of approximately 13%, while the square resistance was found to decrease more significantly. For the electrical conductivity measurements, SWCNT mat samples of 1 mm width were placed on top of two copper electrodes with a gap between of 1 mm. An ethanol droplet added to the sample initially resulted in a sudden increase in the resistance followed by an approximately constant decrease during the ethanol evaporation process. After approximately 3 min, the resistance decreased to between 1.8 and 7.2 times lower than the original value (Table 3). This significant decrease in resistance is likely explained by the SWCNT film densification, increased inter-tube contact and, consequently, an improvement in the percolation between SWCNTs. It is worth noting that the thermal compression integration process of SWCNT mats into polymer film did not cause significant changes to the electrical conductivity. The relationship between square resistance and optical transmittance for SWCNT mats with different thicknesses integrated into PE films are presented in Fig. 4a. For the optical transparency investigations, an uncoated pristine polymer film was used as a reference.

Since one of the potential applications of SWCNTs is devices based on cold electron field emission, we carried out measurements to demonstrate the applicability of SWCNT/PE film for such purposes. The procedure of the measurements is described

Fig. 2. (a and b) TEM images of a sandwich PE/SWCNT/PE structure.

Fig. 3. Demonstration of SWCNT mat densification: SEM images of (a) the as deposited SWCNT mat and (b) the mat after treatment with ethanol.

Table 3
Effect on resistance of densifying SWCNT mats of different thicknesses with ethanol

<table>
<thead>
<tr>
<th>Layer thickness before ethanol (nm)</th>
<th>24</th>
<th>35</th>
<th>100</th>
<th>500</th>
<th>2930</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square resistance before ethanol (Ω/□)</td>
<td>101700</td>
<td>17860</td>
<td>9400</td>
<td>4950</td>
<td>634</td>
</tr>
<tr>
<td>Square resistance after ethanol (Ω/□)</td>
<td>32000</td>
<td>3775</td>
<td>1860</td>
<td>690</td>
<td>350</td>
</tr>
<tr>
<td>Resistance decrease</td>
<td>3.2</td>
<td>4.7</td>
<td>5.1</td>
<td>7.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>
in [6]. Fig. 4b shows the dependence of the current density against the electric field strength obtained during 10 runs. As one can see that the SWCNT/PE film exhibits a low field threshold of about 1.2 V/μm. Another advantage of the film is the presence of a clear current plateau, which is valuable for, for instance, flat screen displays, since the variation of the electric field between 1.7 and 2.7 V/μm does not lead to a significant change in the electron emission. Consequently, more variation is allowable in the component manufacturing process.

Another important and useful property of our SWCNT/PE films is their flexibility. The SWCNT/PE films were found to be bendable and could be repeatedly rolled and unrolled while retaining their transparency, conductivity and field emission properties (Fig. 5).

In summary, we have demonstrated a simple and efficient one step integration process for transferring SWCNT mats into PE thin films. These SWCNT/PE thin films have exhibited good optical transparency and conductivity as well as high mechanical flexibility. The electrical conductivity of the SWCNT mats was significantly improved by ethanol densification. Cold electron field emission measurements from a SWCNT/PE film showed a low field threshold and revealed the presence of a clear current plateau at electric field strengths between 1.7 and 2.7 V/μm.

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