The production of a flexible electroluminescent device on polyethylene terephthalate films using transparent conducting carbon nanotube electrode

Mun Ja Kim, Dong Wook Shin, Jin-Young Kim, Shang Hyeun Park, In taek Han, Ji Beom Yoo

1. Introduction

Transparent conducting films (TCF) comprised of carbon nanotube (CNT) composites (CNT-TCF) have attracted considerable interest from many researchers as a possible way of replacing fragile and heavy oxide TCF such as indium tin oxide (ITO) [1,2]. The CNT-TCF is particularly attractive because the electrical properties can be maintained even after bending and distortion [3]. CNTs are electrically and thermally conducting, strong, and chemically stable [4–7]. These features of CNTs have been utilized as an electron injection and transfer layer in flexible inorganic electroluminescent (EL) devices, which can be fabricated using powder phosphor processes and a CNT-TCF. TCF formed on polyethylene terephthalate (PET) substrates using CNTs may be a replacement for ITO [3,8–10]. However, in use of CNTs based TCF, several obstacles, such as bundle formation or aggregation of CNTs due to the mutual interactions between CNTs and poor adhesion of CNTs to PET substrates, need to be overcome before these films can be used commercially. The properties of the substrate surface can be modified using various chemical radicals. The modified surface improves the dispersion of CNTs on the substrate and provides suitable adhesion of the CNTs to the substrate [11].

As a feasibility study of EL devices using CNT-TCF, this study designed two different structures with a glass substrate and CNT-TCF, and analyzed the characteristics of the resulting EL device. EL devices are a source of plane light, where uniform luminescence is obtained over an entire area under an electric field [12]. Inorganic EL has advantages over organic...
EL in terms of stability and reliability as well as image quality and simple manufacturing process. Nevertheless, in the case of the film type, previous studies have reported cost, screen size, and low luminance as technological barriers [13,14]. One problem with powder phosphor EL devices is the essential high power consumption caused by the binder materials used in the process of making the phosphor layer [15]. However, it is easier to make a large size screen with a powder phosphor for mass production than with film type processes.

This study focused on the fabrication of a flexible EL device. The CNT-TCF was applied as a flexible substrate. Driving the flexible EL device, we characterized the relationship between the EL brightness and quality of CNT-TCF. This paper addresses the efficiency of CNT-TCF for device performance in terms of low power consumption and EL brightness enhancement.

2. Experimental

2.1. Preparation of CNT solution

The surface of single-walled CNTs (Carbon Solutions, Inc. product name: AP-SWNT [16]) was functionalized using a SDS (sodium dodecyl sulfate, \( \text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na} \)) based on water. The single-walled CNTs of 1–7 mg and 1 wt.% aqueous solution of SDS (10 g of SDS in 990 ml of deionized water) was mixed and treated sonication for approximately 1 h to disperse the CNTs. The mixture was centrifuged at high speed, approximately 12,000 \( \times g \) (11,731 rpm), for 20 min to separate the carbon impurity and residual catalyst from the CNTs. The suspended solution was sonicated. The same process, including centrifugation and sonication, was repeated 4 times to obtain a well dispersed CNT solution. The separation of individual CNT from a bundle of CNTs was achieved [17] and the surface of the CNT was functionalized uniformly [18,19]. The surfactant SDS molecules are adsorbed to the surface of the CNT, forming a monolayer so that CNTs were uniformly dispersed [17,19].

2.2. Formation of CNT film

CNT-TCF was formed on the PET film by filtering and transferring [20]. In order to produce a TCF using CNT, the prepared CNT solution was diluted three times with water. By washing off the residual surfactants in flowing water and blowing away the remaining droplets from the CNT-TCF on PET film, it was expected that the residual SDS could be removed from the CNT film. Different amounts of the CNT solution ranging from 0.9 to 1.6 ml was filtered through an alumina membrane with a 200 nm pore size (\( \phi = 2 \) inch, Whatman Inc., UK). A CNT film was formed by transferring the CNTs to a PET substrate. An approximately 0.1 mM 3-aminopropyltriethoxysilane (ATS, \( \text{CH}_3\text{Si(OCH}_3)_3\text{NH}_2 \)) solution in hexane was prepared. The ATS is unstable hydrolytically and the PET surface treated with ATS has a hydrophilic property. This can help easy transfer CNT-TCF to the PET film with better wettability than the alumina membrane. The transparent conducting CNT film was characterized by field emission scanning electron microscopy (FESEM: JEOL, JSM-6700). The sheet resistance \( (R_s) \) and optical transmission properties (% T) of the TCF were measured using a four-point probe (CMT-SR100 N) and UV–visible spectrometer (SCINCO, UV S-2100), respectively.

3. Results and discussion

The EL device had the following components, as shown in Fig. 1A; substrate (glass), ITO electrode, emission layer of phosphors, dielectric layer (SiO\(_2\)) and back side electrode. The flexible EL device was fabricated by replacing a key component of the device by the conducting channel with CNTs, which has superior electrical properties under the distortion of substrates, such as bending and folding. Fig. 1B shows a diagram of the structure for the flexible EL device, in which the ITO coated glass substrate changed to CNT-TCF on the PET substrate. The thickness of the emissive layer and dielectric layer formed on the PET film was approximately 30 and 0.6 \( \mu m \) from the FE-SEM images, respectively. In order to protect the phosphor layer from external moisture, an emissive layer was formed between the CNT-TCF and dielectric layer using a BaTiO\(_3\) powder. The brightness was measured from the electroluminescence toward CNT-TCF of the EL device and as a function of the characteristics of the CNT-TCF.

![Fig. 1 – Structure diagrams of EL device according to substrates change: (A) ITO coated glass substrate (B) transparent conducting film using CNTs on a PET substrate.](image-url)
The transparency (% T) and sheet resistance (R_s) of CNT-TCF samples formed with different amounts of the CNT solution were measured. Table 1 shows the features of 8 films (4 films were pre-treated with the ATS solution the other 4 films were not treated with ATS). The amount of filtered CNT solution was 0.9, 1.0, 1.5, and 1.6 ml, which are expressed as film numbers 1, 2, 3, and 4, respectively. There was no significant difference in transmission or R_s between the films before and after the ATS treatment. By dipping into an ATS solution, an amino (NH2) group formed on the surface of the PET film, which makes it more hydrophilic. A tape test (put a general 3 M tape on the CNT film and then detached) was performed to examine the adhesion of the CNT film to the substrate. Although CNT film on PET film without ATS treatment was scratched out, CNT film on PET film with ATS treatment did not show any change in surface morphology after tape test. The adhesion properties of the CNTs to the substrate were improved by the ATS treatment.

As shown in Fig. 2, the transmission at 550 nm and R_s tend to decrease with increasing amount of the CNT solution. The difference in (% T) and R_s between each film may be attributed to finer points, such as the degree of contact between the CNTs and the dispersion of CNTs over the PET substrate.

Fig. 3A shows the brightness of the EL devices as a function of the driving voltage at a frequency of 400 Hz. Fig. 3B shows the brightness of the EL devices as a function of frequency under an applied voltage of 50 V. The symbols in Fig. 3 correspond to the films shown in Table 1. ‘3A’ denotes film number 3 that had been treated with ATS. A reference denotes EL device made on ITO coated glass using the same process. The sheet resistance of ITO on glass was approximately 20 ohm/sq. According to Zalm[13], if the initial brightness is ignored, the brightness increased linearly with increasing applied voltage. As shown in Fig. 3A, the plots were linear over 50 V. Chander et al.[15] reported a mixed behavior and deviations from a linear relationship at frequencies lower and higher than 24 kHz. From the results shown in ‘3’ and ‘3A’, the adhesion of the CNT to the substrate had an impact on the brightness of the EL device. The CNT-TCF without the ATS treatment, ‘3’ did not make a significant contribution to brightness of the EL device.

The transparency (% T) and sheet resistance (R_s) of CNT-TCF formed with different amounts of the CNT solution before and after ATS treatment.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Film no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>% T (at 550 nm)</td>
<td>With ATS</td>
<td>78.0</td>
<td>72.6</td>
<td>62.3</td>
<td>59.3</td>
</tr>
<tr>
<td>R_s (ohm/sq)</td>
<td>w/o ATS</td>
<td>78.5</td>
<td>74.8</td>
<td>62.1</td>
<td>59.7</td>
</tr>
<tr>
<td></td>
<td>With ATS</td>
<td>546.5</td>
<td>397.1</td>
<td>235.2</td>
<td>215.9</td>
</tr>
<tr>
<td></td>
<td>w/o ATS</td>
<td>581.2</td>
<td>336.7</td>
<td>211.5</td>
<td>223.7</td>
</tr>
</tbody>
</table>

The process for making the TCF from CNT by filtering and transferring needs to be performed skillfully without scratching. First of all, the morphology of the CNT-TCF has a major influence on brightness; a scratch can create an electric short circuit. The EL device of ‘1A’, ‘2A’, and ‘4A’ show the electric shortage under the formation of an electric field. From the results shown in ‘3’ and ‘3A’, the adhesion of the CNT to the substrate had an impact on the brightness of the EL device. The CNT-TCF without the ATS treatment, ‘3’ did not make a significant contribution to brightness of the EL device.

There are many finer control points, such as resistance between the CNTs, the CNT and substrate, the CNT-TCF and phosphor layer, and phosphor layer and dielectric layer, which affect the properties of flexible EL devices made using a CNT-TCF. Reducing these resistances and providing a greater likelihood of an electron being excited for light emission can improve the brightness of the inorganic powder EL device.

Fig. 5A shows a photograph of the EL device using CNT-TCF. The left side of the film shows the transparency of the light emitted from the phosphor layer because brightness was taken from electroluminescence toward the CNT-TCF of the EL device, as shown in Fig. 1B. The CNT-TCF was efficient in electron injection and as a transfer layer at a flexible EL device. As shown in Fig. 3, the brightness of the EL device using CNT-TCF was approximately 44 cd/m² at 150 V–400 Hz. In addition, the brightness as a function of frequency at 50 V was similar to that of ITO coated glass below 24 kHz. From the ‘3A’ device, a brightness of 96.8 cd/m² was obtained at 28 kHz.

The transparency (% T) and sheet resistance (R_s) of CNT-TCF formed with different amounts of the CNT solution before and after ATS treatment.
CNT film (film number is 3, ATS treated, in Table 1) used in the electrode part. The right side shows the completed device, which appears darker than the left side. The emission can be created from both sides of the EL device if ITO is deposited as a back electrode. Fig. 5B shows a photograph of the electroluminescence of the flexible EL device using CNT-TCF shown in (A): emitted at 400 Hz, 100 V. The image was captured as a function of the frequency of the driving voltages from 400 Hz. The image in Fig. 5B shows uniform emission over the entire surface.
4. Conclusions

A TCF using CNT composite was introduced in an attempt to fabricate a flexible EL device. The CNT-TCF was formed by filtration of CNT solution and was transferred to the PET film. The CNTs were dispersed in the solvent using SDS. The PET surface was functionalized with ATS to enhance the adhesion of CNTs to the PET film. For the completion of the EL device, a commercial EL green powder phosphor with a particle size <20 \( \mu \)m was used. An emissive layer was formed between the CNT-TCF and dielectric layer using BaTiO\(_3\) powder to protect the phosphor layer from external moisture. The brightness was taken from the electroluminescence toward CNT-TCF of the EL device. The flexible EL device using CNT-TCF has a transparency, sheet resistance of 62% and 235 ohm/sq, respectively, and showed a brightness of 96.8 cd/m\(^2\) at 28 kHz and 50 V. The results showed that the morphology of the CNT-TCF can have a significant effect on brightness of the resulting EL device; a lack of CNT film uniformity can create an electric shortage. Increasing the transparency of CNT-TCF or the probability of exciting an electron for light emission in the EL device can improve the brightness of flexible inorganic powder EL devices.

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REFERENCES