Physical Change of Transparent Film Heaters Based on Single-Walled Carbon Nanotubes in High Temperature Environment

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Carbon nanotube (CNT) is a cylindrical carbon nanostructure with good transport properties along tube's axis. As one approach of practical use, CNT networks are made and their application to many areas is investigated. In particular, since single-walled carbon nanotubes (SWCNTs) are very slender, network of SWCNTs can be transparent keeping the inherent transport characteristics. The transparent conducting film (TCF) has been studied for use as electrodes in photovoltaics, organic light-emitting diodes, touch screens, sensors, transistors, and speakers. Recently, we reported the possibility of creating a transparent heater using CNT-TCF [1]. In such a heater, we must consider various physical aspects, which affect each other during the heating of the CNT-TCF. Detailed research into the thermal characteristics of CNT-TCFs is essential if they are to be commercially used as transparent heaters.

In this research, we investigated the thermal behavior of transparent film heaters (TFHs) made of single-walled carbon nanotubes (SWCNTs). The temperature dependence of the electrical resistance of the TFHs heated by Joule heating was examined. The change in physical properties of the TFHs due to heating was investigated with an analysis of Raman and transmittance spectra.

We fabricated the TCF by using the spray coating method. We dispersed SWCNTs in deionized water with 1 wt% sodium dodecyl sulfate (SDS) and sonicated for several hours. The concentration of the SWCNT solution was 1 μg/ml. We sprayed the SWCNT solution on a glass substrate to form the TCF. The size of the glass substrate is 50 mm × 50 mm × 0.5 mm. As a result, we made TCFs with transparency of about 70 % at 550 nm. The sheet resistance of the TCFs was in the range of 130~160 Ω/sq. Finally, on the TCF, we formed electrodes by using silver paste to make a low-resistance electrical contact. We applied the voltage difference of 60 V across the electrodes by using a DC power supply (Agilent E3649A). We measured the voltage difference and the surface temperature of the TCF by using a data acquisition unit (Agilent 34970A) and monitored the electrical current through the TCF by using a current meter (Fluke 189). For temperature measurement, we used T-type thermocouples. We calculated the electrical resistance by dividing the applied voltage difference by the measured current. To analyze the Raman spectra of the TFHs before and after heating, Raman spectroscopy with wavelength of 633 nm (inVia, Renishaw) was used to detect changes in the RBM, D, and G modes. We measured the optical transmittance by using the absorption spectroscopy (Optizen 2120UV Plus).

After heating and leaving the samples at room temperature for several days, we measured the resistances of the films. The results are shown in Table 1. There was no significant change when the film was heated to 150°C; the resistance changes were too small. However, heating to 200°C did change the resistance. After recovery, the TFH resistance had increased by about 10%. Moreover, when the temperature was increased to 300°C, the resistance, even after a few days of recovery, increased significantly by over 300%.

To determine the reason why the resistances changed permanently above 200°C, we captured Raman spectra with excitation energy of 633 nm; the result is shown in Fig. 1. Figure 1 compares the results for unheated (pristine) samples, samples heated to 65°C, and samples heated to 200°C. For the pristine and samples heated to 65°C, the peaks in the RBM, D, and G bands did not change, demonstrating that there was no physical change caused by low-temperature heating. On the contrary, Joule heating of the TFH to 200°C caused a definite change in the physical aspects. The semiconducting peak in the RBM mode disappeared, and the peak in the G^- band increased. This means that some of the semiconducting nanotubes were removed. In the D band, several peaks, except for 1340 cm^{-1}, which denotes defects on the carbon lattice structure, were significantly reduced. A previous report indicated that a CNT is burned out when a large current is applied [2]. If the connection between electrodes includes metallic and semiconducting nanotubes, the metallic nanotubes are broken down first. According to the stepwise increase of the current, they could create a semiconducting device. However, we obtained unexpected results by heating the TFH above 200°C. This behavior requires further detailed research.

We heated the TFH to temperatures greater than 300°C and found that the optical morphology of the TCF definitely changed as shown in Fig. 2. In the region 2, the temperature was maximum and greater than 360°C. The higher temperature made the region 2 of the TCF more transparent. When we measured the transmittance of the TFH sample before and after the experiment, the transparency of region 2 improved significantly from 69.7% to 85.7% at 550 nm. On the other hand, the transmittance of the regions 1 and 3 of the TCF sample changed very little.

We are developing an explanation on the mechanism underlying the observed phenomena. This study would improve understanding of the heating effect on the physical properties of the transparent conducting film using SWCNTs which could be a good candidate for the heater in many applications requiring both heating function and transparency.

References

[1] Yoon, Y. H., Song, J. W., Kim, D., Kim, J., Park, J., Oh, S. and Han, C.-S., *Advanced Materials*, **19** (2007) 4284-4287.
[2] Collins, P. G., Arnold, M. S. and Avouris, P., *Science*, **292** (2001) 706-709.

Figures

Table 1 Permanent resistance change according to maximum heating temperature.

Maximum heating temperature (°C)	Electrical resistance (Ω)	
	Before heating	After heating
65	135.5	137.2
100	138.0	133.6
150	139.0	133.5
200	135.2	147.8
300	136.8	497.6

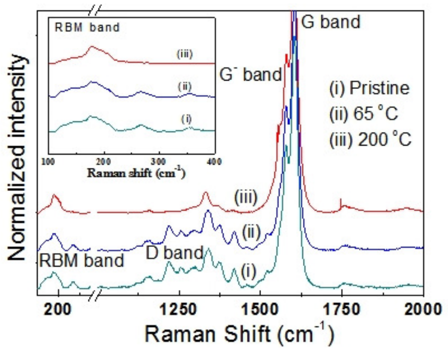

Fig. 1 Raman spectra of SWNT thin films at an excitation energy of 633 nm.

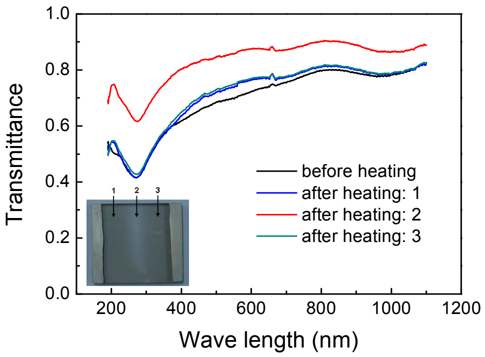

Fig. 2 Transmittances of the TFH heated above 300°C.