

Temperature Dependent Resistance of Multi Wall Carbon Nanotube By Inkjet Printing

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Abstract

We present the fabrication and the characterization of temperature-sensitive resistors made by inkjet printed multi-wall carbon nanotube (MWCNT) network films. Centrifuged aqueous solutions of with 0.5 wt.% MWCNT was used to perform a stable drop ejection without nozzle clogging. Single nozzle piezoelectric inkjet heads with 50 micron inner diameter were used to print resistor patterns with a size of 0.3×5 mm up to 16 layers on Pyrex glass substrates. The samples were annealed in a tube furnace with or without air at various temperatures. High density network films of MWCNT were fabricated. All the samples show linear I-V relationship and the conductance was almost proportional to the number of layers. The resistance decrease with the annealing temperature slightly. For the samples annealed in the air, the temperature dependence on the resistance was relatively stable.

1. Introduction

Carbon nanotubes(CNTs) show lots of interesting material properties such as high mobility, good mechanical strength, and high current density and have been utilized in a number of different devices for several years.[1-4]

Recently, the bolometric infrared photoresponse of single wall CNT (SWCNT) films have been reported.[5,6] SWCNTs exhibit a very high temperature coefficient of resistance (TCR), especially in a very low temperature range but are also very sensitive to the other factors like ambient gas and visible light. A large and reliable TCR of the sensing material is indispensable for the practical sensor applications. By using multi wall CNTs(MWCNTs) instead of SWCNTs, very stable electrical properties can be expected without preselection of metallic / semiconducting nanotubes.

But the earlier studies generally used large CNT films in order to measure the photoresponse. It is required for mass production to fabricate smaller suspended patterns of CNT film on a substrate for thermal isolation.

The mechanical manipulation of individual CNTs[7] and the growth of CNT bundles on pre-patterned substrates using chemical vapor deposition methods (CVD)[8] are used for the demonstration of a variety of novel devices. But these processes are not scalable and cost-effective in many applications. Recently, inkjet printing technology enables the uniform deposition of electronic materials on a large substrate and several groups have applied the inkjet printing of CNTs.[9-14]

In our work, we present the fabrication and the characterization of temperature sensitive resistors using inkjet printed MWCNT network films.

2. Experimental details

2.1 Ink preparation

MWCNTs with a diameter of 10 ~ 15 nm and a purity of more than 95% by thermal CVD process purchased from Hanwha Nanotech were used as a initial material to produce a solution for inkjet printing process. A horn type sonication was followed to control the length of the MWCNTs for a better printing stability and the CNTs are dispersed in de-ionized water with various surfactants like sodium dodecyl sulfate(SDS). So the aqueous solutions of MWCNT with 0.5 wt.% density and 5 cP of viscosity were produced and all the solutions are filtered with a sieve before inkjet printing to prevent nozzle clogging. Several solutions were tested and we select one of them represent the most stable drop ejection for patterning process.

2.2 Sample preparation

The printing of MWCNT network film was carried out using a commercial inkjet printing system UJ-200 from Unijet, Korea equipped with a piezoelectric single nozzle head from MicroFab, USA with 50 micron inner diameter as shown in figure 1.

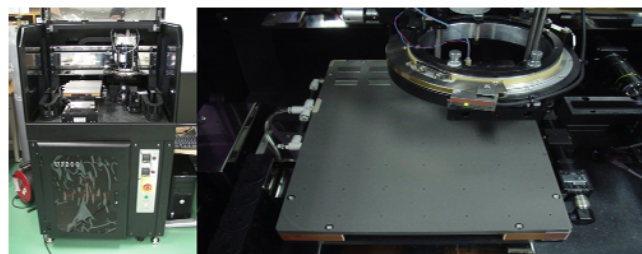


Figure 1. Printing system, UJ-200

The waveform to the head was optimized to achieve a stable drop ejection without satellite formation and the ejection frequency was 1 kHz.

Pyrex glass substrates were cleaned by piranha solution to remove all the contaminants before inkjet printing process and no additional surface treatment was applied to the substrates.

Every layer of MWCNT network films are printed four times to obtain uniform MWCNT network films. Each color dot in figure 2 was printed with enough spaces to prevent the agglomeration of nearby droplets

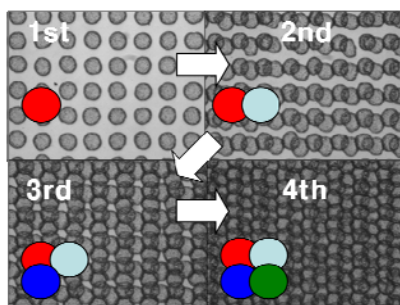


Figure 2. One complete cycle for one layer of MWCNT network film

The actual strip pattern of MWCNT resistor is shown in figure 3. They were printed repetitively and MWCNT network patterns with different thickness are fabricated on the substrates by printing different numbers of layers (1, 2, 4, 8, 16 layers).

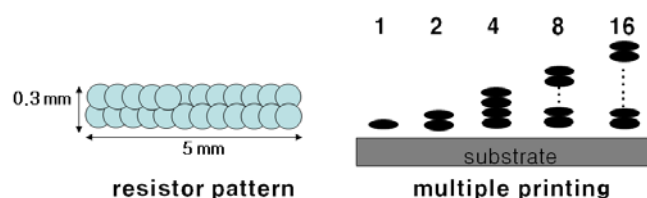


Figure 3. MWCNT resistor pattern and multiple printing

The printed samples were dried at room temperature for one hour after printing and they were annealed in a vacuum or in the air at different temperatures (100, 200, 300, 400 °C). Finally, silver epoxy pastes were dispensed at the ends of each MWCNT strip pattern and cured at room temperature in order to connect the multimeter.

2.3 Measurement setup

To investigate the temperature dependence on the resistance of a variety of MWCNT network films, we set up a PC-controlled multi-channel resistance measurement system based on a commercial package Labview (National Instruments, USA) with a conventional environmental test chamber (SH-241, Espec, Japan), in which we can measure the resistance of 128 samples simultaneously.

To avoid any influence from the temperature fluctuation of the chamber, every measurement at each temperature step was done after enough soaking time more than 10 minutes.



Figure 4. Temperature dependence characterization system

3. Results and Discussion

Figure 5 shows optical images of the printed MWCNT network patterns with different number of layers. High density

MWCNT network films were obtained by single printing process. The thickness of the single printed films is not uniform as shown in figure 6(left) but the films with multilayers showed better uniformity. We can see clearly individual MWCNTs after the annealing process by field-emission scanning electron microscope in figure 6(right)

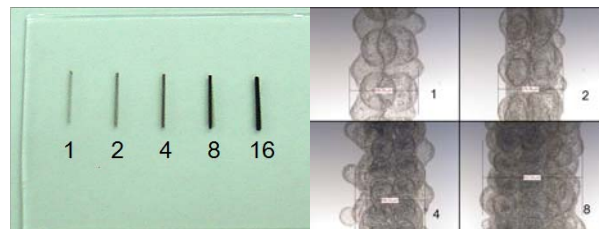


Figure 5. MWCNT network film pattern with different number of layers

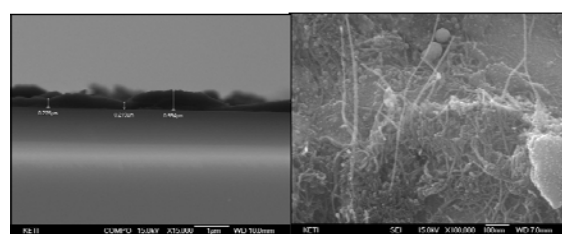


Figure 6. Microscopic structure of MWCNT network film

All the samples show linear I-V curves as shown in figure 7, which is same as individual MWCNT's characteristics.

The conductance was roughly proportional to the number of layers as shown in figure 8, regardless of annealing condition such as temperature or atmosphere, which also is expected by simple thickness to conductance relation of bulk material. Annealing of the printed substrate in the air at 400 °C burn out all the MWCNTs on the substrate.

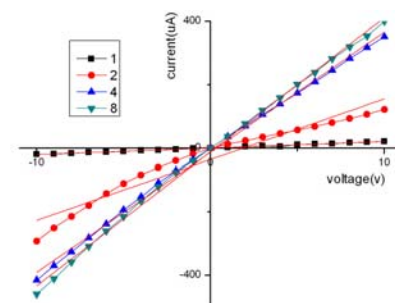


Figure 7. I-V characteristics of MWCNT network film

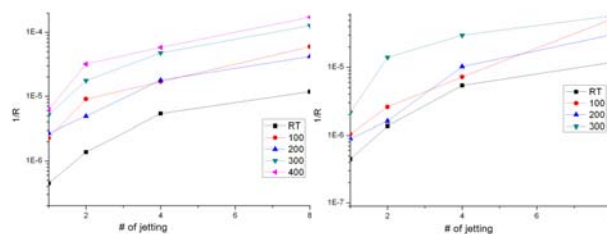


Figure 8. Conductance - number of layer(left : vacuum, right: air)

The resistance decreases with the annealing temperature slightly regardless of the number of layers. The resistance of the

sample annealed in vacuum generally showed lower value, and it is considered that partial oxidation of MWCNTs occurred during annealing process in the air.

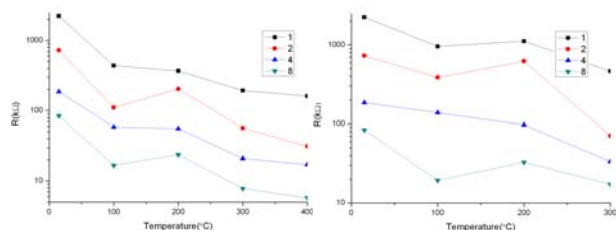


Figure 9. Resistance versus annealing temperature(left : vacuum, right: air)

The temperature dependence curves on the resistance of a variety of MWCNT network films by inkjet printing are shown in figure 10 and 11. Temperature-resistance relationship is not affected by the number of layers but by annealing condition much.

The samples annealed in the air show a constant negative TCR of about $-0.1 \sim -0.3 \text{ \%}/\text{K}$ within the temperature range measured but those annealed in a vacuum show a very low negative or even positive TCR above room temperature. So the prior processes can be considered to be more suitable for general sensor application.

The samples annealed in a vacuum showed plus or minus values of TCR depending on the temperature. One of possible assumptions is that the residue of the organic additives including the surfactant in the solution cannot be decomposed completely even after the annealing process without oxygen since the electrical properties of individual MWCNT doesn't change much below 400°C in a vacuum.

For the samples annealed in the air, a decrease of TCR at higher temperature was observed. It can be attributed to the increasing contact resistance between individual MWCNTs. The relatively smaller value of the TCR above room temperature than that of the literature[15] suggests that the optimization of a solution and the annealing process will be required for further enhancement.

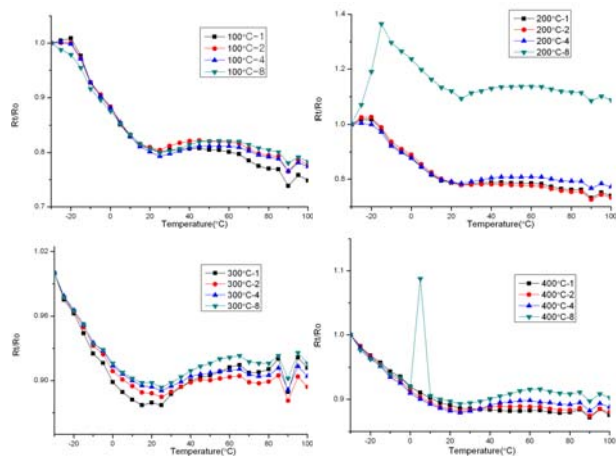


Figure 10. Temperature dependence on the resistance(annealed in vacuum)

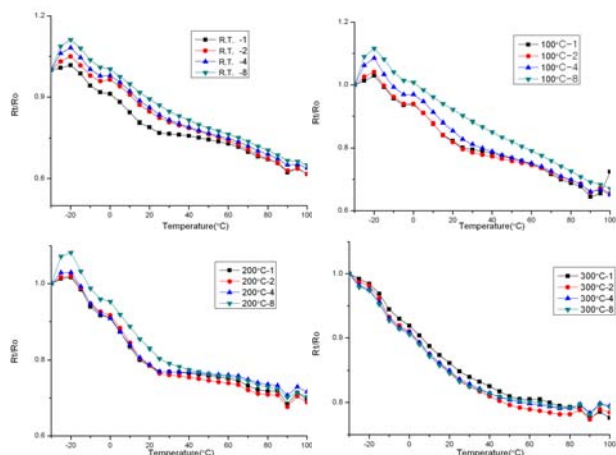


Figure 11. Temperature dependence on the resistance(annealed in the air)

Conclusions

Temperature dependence on the resistance of inkjet printed MWCNT network film has been investigated. Annealing conditions like temperature and ambient affect the behavior much and MWCNT films annealed in the air show relatively stable negative TCR of about $-0.2 \text{ \%}/\text{K}$.

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K. I. Lee received the B.Sc. and M.Sc. degrees in physics from Seoul National University, Seoul, Korea, in 1997. He then joined Korea Electronics Technology Institute, Seongnam, Korea and is currently a managerial researcher in Green energy research center. His field of research has been in the area of MEMS-based nanotechnology. His focus is in the direct patterning technology such as inkjet printing with nano-material for an environmentally friendly fabrication process.