**Journal of Experimental Nanoscience**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t716100757

# Fabrication of humidity sensors by multi-walled carbon nanotubes

Jeff T. H. Tsai[a]; Chih-Cheng Lu[b]; Jason G. Li[a]
[a] Institute of Electro-Optical Engineering, Tatung University, Taipei 10452, Taiwan, ROC [b] Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan, ROC

Online publication date: 07 July 2010

**To cite this Article** Tsai, Jeff T. H. , Lu, Chih-Cheng and Li, Jason G.(2010) 'Fabrication of humidity sensors by multi-walled carbon nanotubes', Journal of Experimental Nanoscience, 5: 4, 302 — 309
**To link to this Article: DOI:** 10.1080/17458080903513300
**URL:** http://dx.doi.org/10.1080/17458080903513300

*Journal of Experimental Nanoscience*
Vol. 5, No. 4, August 2010, 302–309

# Fabrication of humidity sensors by multi-walled carbon nanotubes

Jeff T.H. Tsai[a]*, Chih-Cheng Lu[b] and Jason G. Li[a]

[a]*Institute of Electro-Optical Engineering, Tatung University, Taipei 10452, Taiwan, ROC;* [b]*Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan, ROC*

(*Received 10 September 2009; final version received 26 November 2009*)

Humidity sensors have multi-walled carbon nanotubes (MWNTs) as the sensing material is demonstrated. The sensor was fabricated on a silicon dioxide coated silicon wafer with metal electrodes. MWNTs were deposited and interlinked with the electrodes by means of the dielectrophoresis technique. The sensing device has the function of a hygrometer when measuring resistance variations to the local relative humidity percentage (RH%) through MWNTs. By measuring the MWNT resistances, we find that higher RH% results in a decrease of conductivity. The results indicate that electron transports in MWNTs are affected by water molecules adsorption on the outermost nanotube surface. A miniature thermocouple sensor was also fabricated and integrated with the humidity sensor. This allowed us to simultaneously sense environmental humidity and temperature. Hence, accurate humidity measurements were achieved with this prototype by calibrating the electrical resistance and temperature levels to carry out the tests with the humidity percentages.

**Keywords:** carbon nanotubes; humidity sensor; dielectrophoresis



## 1. Introduction

Carbon nanotubes (CNTs) are molecular-scale tubes constructed by graphitic carbon. The process of folding a single graphene layer into a carbon cylinder as a single-walled carbon nanotube (SWNT) or of folding many layers of graphite into a multi-walled carbon nanotube (MWNT) gives CNTs unique electrical and mechanical properties. The remarkable electronic properties of a SWNT are owing to its metallic or semiconductive behaviour arising from the structure of different chiral vectors. Hence, it can be used as an active semiconductor material for electronic device applications. Tans et al. [1] found that two types of material properties are present in CNTs. Linear current–voltage and no dependence on the gate voltage of the field-effect transistor (FET) present in the active material are metallic CNTs, while the asymmetric dependence of conductivity on the gate voltage implies that the active CNT is semiconducting [1]. The CNT FET and complex logic circuits were also demonstrated [2–4]. A p-type metal-oxide-semiconductor (PMOS) inverter and an n-type metal-oxide-semiconductor (NMOS) inverter on a CNT doped with

*Corresponding author. Email: thtsai@ttu.edu.tw

ISSN 1745–8080 print/ISSN 1745–8099 online

DOI: 10.1080/17458080903513300
http://www.informaworld.com

potassium have been demonstrated for the basis of an integrated circuit. The assembly of these transistors to complete a complementary metal-oxide-semiconductor (CMOS) structure has been reported by Liu [5]. Both types of inverters can work at room temperature and possess fair current gains.

CNTs are not only suitable for microelectronic applications, but are also used in sensor applications. Using an SWNT as an oxygen sensor has also been reported, with the device evaluating the oxygen concentration by observing the variation of resistance from the nanotube [6]. Kong used SWNTs as sensing material and combined them with FETs to detect two different class gases: the reducing gas $NH_3$ and the oxidising gas $NO_2$ [7]. Before exposure to these gases, the SWNTs show p-type transistor characteristics. After exposure to the oxidising gas, the gate voltage ($V_G$) shifts to a strong positive, while exposure to the reducing gas shifts the $V_G$ to the negative. This result indicates that the interaction between CNTs and molecular species in the environment may significantly affect the electrical properties of the SWNT. Kim [8] also found that in ambient air, the *I–V* characteristic is significantly affected by water molecules.

## 2. Experiment



The aim of our device fabrication is to generate a large contact area to interlink the MWNTs into a bundle. We first clean the silicon substrate with acetone and IPA in an ultrasonic bath for 5 min to remove any residual particles and grease. We follow this by flushing it in DI water and baking it in a 150°C oven. The substrate then thermally grows to a $SiO_2$ layer, 1000 nm in thickness. The metallisation processes are performed in a vacuum sputtering system. Chromium metal is deposited in a 500 nm layer onto the patterned substrate. The electrode pattern defined on the substrate employs photolithography and lift-off techniques (Figure 1(a)).

In this study, we use commercial MWNTs from Conyuan Biochemistry Technology (Taipei, Taiwan), which have 96.6% purity, an approximate average length of 5–15 μm and a width of 10–20 nm. The MWNTs are dispersed in IPA by means of an ultrasound bath for 1 h and then settled for a couple of days to separate the heavy particles from non-dispersed MWNTs. This is followed by a centrifugation method to break out the tangled CNTs. It is essential to use separated CNTs to interlink electrodes instead of covering the electrode surface with tangled CNTs because tangled MWNTs will not interlink the electrodes properly and will usually give very unstable resistance when measured through electrodes. The alignment of CNTs and other nanowires has been demonstrated by dielectrophoresis (DEP) [9,10]. Hence, we utilise DEP with well-dispersed CNTs to interlink metal electrodes. Several drops of the well-dispersed CNT solution are then transferred onto the centre of the sensing electrodes. The 1 MHz square wave signal is connected to the electrode pads to perform the DEP process. This forces the MWNTs to align directionally across the electrode gaps, as shown in Figure 1(b). The detailed micrograph of the sensing area is shown in Figure 1(c).

To optimise the DEP process, we tried different voltages and frequencies and found that when the external electric field increases, the velocity of CNTs moving towards the electrode increases. Moreover, an unsuitable electrical field and frequency will cause a hydrolysis reaction and destroy electrodes and generate bubbles. This was discovered in 1994 by Washizu [11], who explained that the bubble formation had been generated

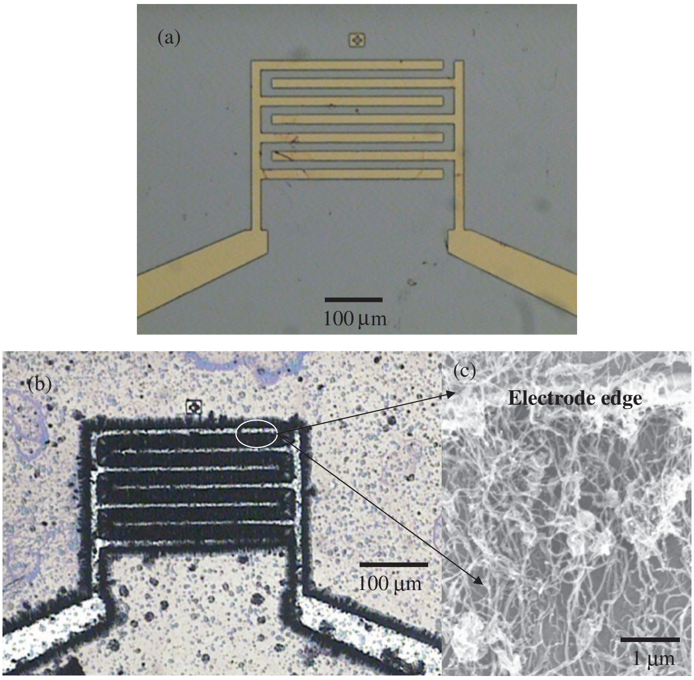


Figure 1. (a) The original electrode after left-off patterning. (b) MWNTs cross-link between electrodes after DEP process. (c) A detailed micrograph of CNTs linking at the electrode.



by the Joule heating of solutions. To avoid such a situation, we optimised the process and found that the input signal has to be maintained at 16 V (peak-to-peak) and at a 1 MHz square wave to enforce the attachment of the MWNTs to the electrode edges. Under such deposition conditions, there is a variation of CNT density to interlinking on the electrodes which gives around 20% deviation from sample to sample when the initial resistance is measured. As the temperature also affects the conductivity of the CNT, a miniature thermal couple was fabricated by depositing two different metals (Cr and Ni in our case) on the same humidity sensor chip. By doing so, the local temperature can be determined by thermocouple as shown in Figure 2.

## 3. Results and discussion

Figure 3 shows one of the output characteristics of our device. This measurement is performed in a plastic desiccator. In order to receive the signal from the sealed plastic desiccator, we use thin metal leads connected to bonding pads on the sensor chip. A Keithley 2410 source-meter with a computational program for data acquisition was used to analyse the device's conductivity. The device was tested under the conditions of 70 and 42% humidity, respectively, for 1 h at a room temperature of 28°C. The results show that the conductivity of the MWNTs is significantly affected by water vapour, indicating that higher humidity doubles the resistance of the device. A more detailed measurement

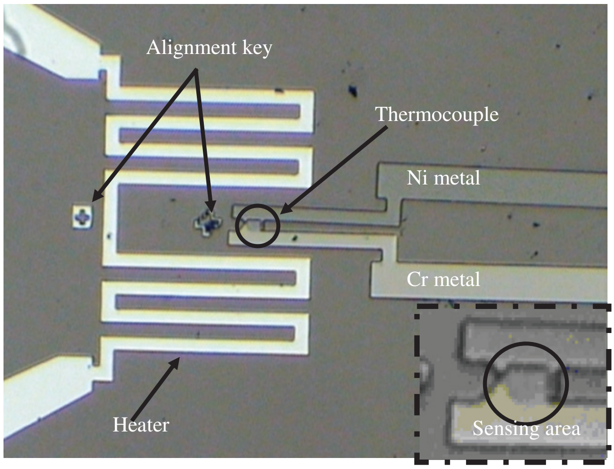


Figure 2. Miniature thermocouple fabricated on the same chip as the humidity sensor.

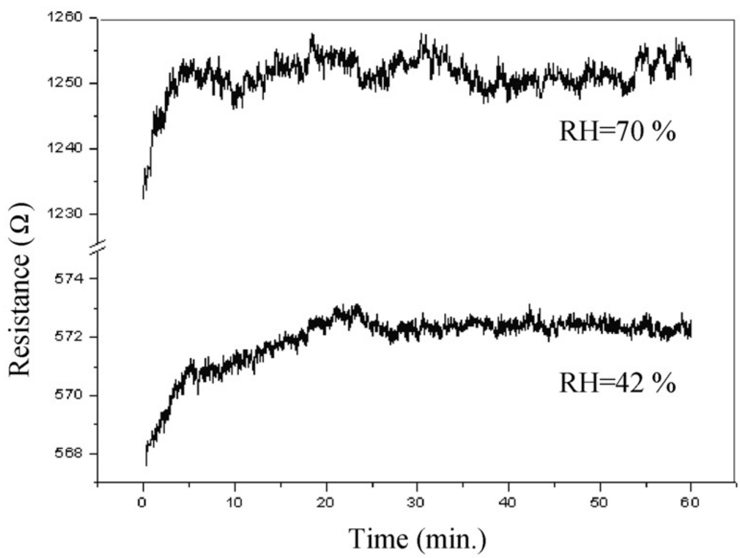


Figure 3. Device resistances over a long period of observation at relative humidity of 70 and 42%.

from another sample, which has less CNT attached, shows that the resistance of the device increases linearly with the humidity, as shown in Figure 4. Zhao et al. [12] simulated the oxidising and reducing gas responses on a SWNT. From their results, they concluded that an oxidising gas will draw electrons out from SWNTs, while a reducing gas will donate electrons. When an SWNT is exposed to an $NO_2$ or $O_2$ environment, the electrical resistance decreases due to an increase in electron concentration. When the nanotubes are switched to $H_2O$ (reducing gas) surroundings, the resistance of an SWNT increases due to the capture of excess electrons. Another possibility for this is due to water molecules

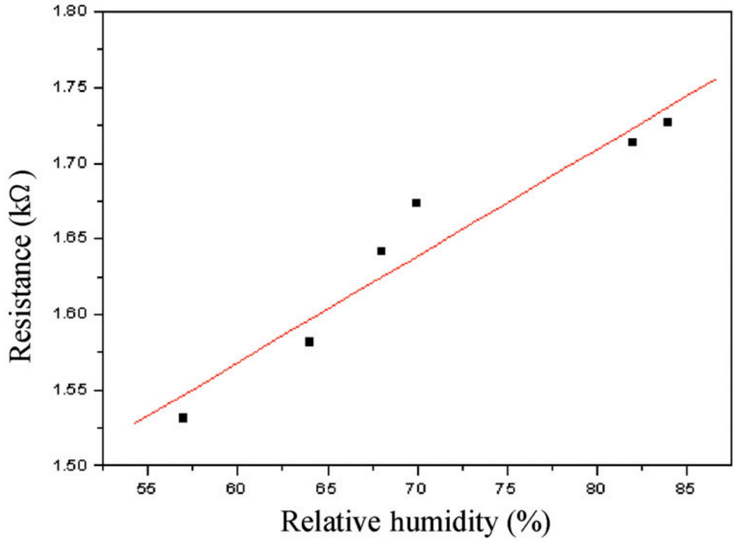


Figure 4. Resistance as a function of humidity for one of the specific sensors gives a response of 13 Ω per RH%.



bridging the interface of the CNT/$SiO_2$ to form charge traps. As Kim [8] reported, they used a suspended SWNT FET and coated the other sample with PMMA to prove that the interface is significantly affected by the *I–V* characteristic. They found that when a sample is placed in a different environment, including ambient air, dry air or vacuum, the hysteresis is significantly changed, especially in the suspended SWNT FET. In other words, the water molecules are concentrated onto the interface of the $SiO_2$ and nanotubes. These water molecules could act as charge traps and influence conductivity [13].

From our results, the phenomenon of MWNT electrical resistance by means of water adsorption was also observed. This may be attributed either to the carrier compensation of the reduction gas on the outermost layer of the MWNT or to the existence of water molecules on the interface between the CNTs and $SiO_2$ layer. To verify the mechanism of humidity affecting the conductivity of the CNT, we measured the resistance from non-overlay MWNTs directly by a nanometer scale electrode gap which is fabricated by electron beam lithography. Both ends of these nanotubes were firmly buried under the Pt contact pad as shown in Figure 5. The variation in environmental humidity does not affect the resistance of the nanotubes, which exhibit a linear *I–V* behaviour with electrical resistances in the range of 30–50 kΩ. This demonstrates the metallic nature of the MWNT. Compared to the previous large-scale sensor device, which interlinked between nanotubes, the electron here was transported through a single CNT from one end to the other directly to avoid it having to hop from one tube to another. Therefore, we can conclude that the variations of resistance in MWNTs may originate from water absorbing on the tube-to-tube interface, thereby preventing the electron from hopping and increasing the resistance of the system.

We also tested this device as a three terminal structure by applying a voltage on the silicon substrate as the gate bias. We attempted to employ the gate voltage to modulate

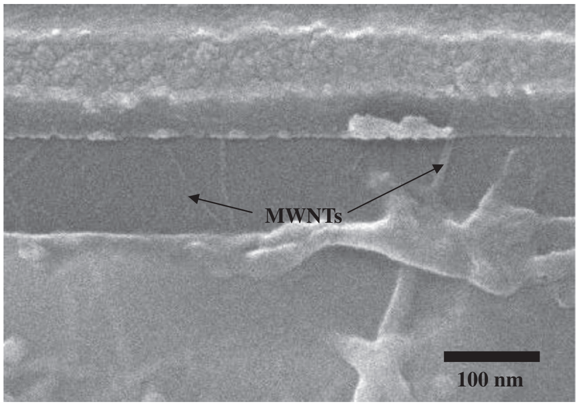


Figure 5. Electron beam lithography patterned small gap device, CNTs in firm contact on the electrodes.

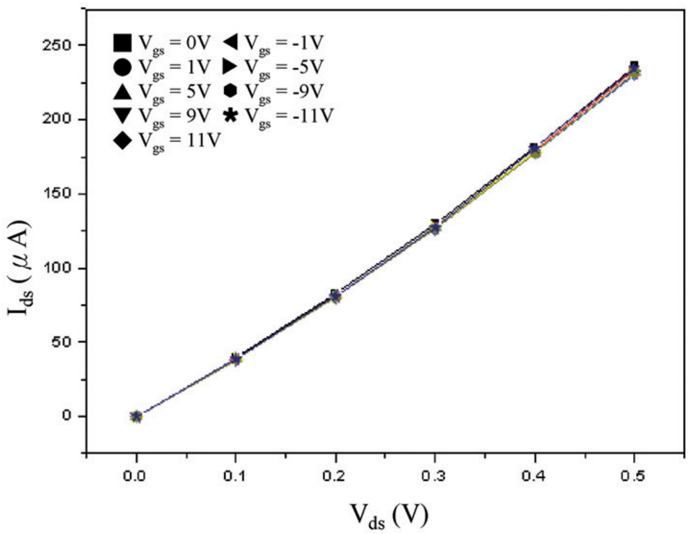


Figure 6. Drain current vs. drain voltage curves of the device upon the interchange of the gate voltage.

the variation of the current. Figure 6 shows that when the applied $V_G$ is between $-15$ and $+15$ V, the source to drain has very little dependence on the gate voltage whether the $V_G$ is positive or negative. In fact, the humidity versus $I_{DS}-V_{DS}$ shows the same characteristic (thus no dependence on the gate voltage). Hence, it is difficult to use the gate voltage to modulate the constant drain current in order to read out the environmental humidity.

As temperature also strongly affects CNT conductivity, we performed another experiment to calibrate humidity. We used a heater to heat up the device and observed the device's responses across a range of temperatures from room temperature to 90°C. It

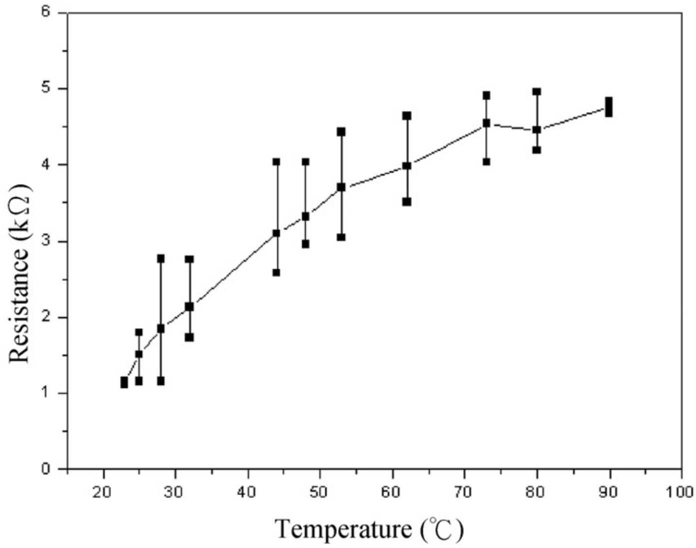


Figure 7. The device calibrated by its resistance vs. temperature using a K-type thermocouple closely attached to the sensing area.



should be noted that the amount of water vapour depends on ambient air at a particular temperature. Therefore, environmental temperature is a key issue to RH%. Here, we control the RH% to be less than 10% so as to eliminate the effect of water. Electric resistance value versus temperature is presented in Figure 7. The result shows the approximate linear variation of resistance with temperature, suggesting that the MWNTs are functioning as metals. We, therefore, calibrated the RH% to the required temperature using the miniature thermocouple to present more actual RH% in any temperature regime.

## 4. Conclusions

Our experiments show the linear response of humidity and temperature to the conductivity of CNTs. This sensing characteristic indicates that MWNTs can be utilised as humidity sensors. The electrical property of MWNTs is significantly affected by water adsorption and can be used to fabricate to a single-chip humidity sensor. We also found that the MWNT in our device had a metallic characteristic and that it absorbs water molecules in the tube-to-tube interface, thereby reducing the electrical conductivity. Therefore, the carrier concentration decreases proportionally to the concentration of the water adsorbing on the bundles of the nanotube, but does not interfere the carrier transport in a single MWNT.

## Acknowledgements

Financial support for this research from the National Science Council, Taiwan, under grant NSC 97-2112-M-036-001-MY3, is gratefully acknowledged.

## References

[1] S.J. Tans, A.R.M. Verschueren, and C. Dekker, *Room-temperature transistor based on a single carbon nanotube*, Nature 393 (1998), pp. 49–52.
[2] R. Martel, T. Schmidt, H.R. Shea, T. Hertel, and Ph. Avouris, *Single- and multi-wall carbon nanotube field-effect transistors*, Appl. Phys. Lett. 73 (1998), pp. 2447–2449.
[3] A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, *Ballistic carbon nanotube field-effect transistors*, Nature 424 (2003), pp. 654–657.
[4] S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and Ph. Avouris, *Carbon nanotubes as Schottky barrier transistors*, Phys. Rev. Lett. 89 (2002), p. 106801.
[5] X. Liu, C. Lee, and C. Zhou, *Carbon nanotube field-effect inverters*, Appl. Phys. Lett. 79 (2001), pp. 3329–3331.
[6] P.G. Collins, K. Bradley, M. Ishigami, and A. Zettl, *Extreme oxygen sensitivity of electronic properties of carbon nanotubes*, Science 287 (2000), pp. 1801–1804.
[7] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, and H. Dai, *Nanotube molecular wires as chemical sensors*, Science 287 (2000), pp. 622–625.
[8] W. Kim, A. Javey, O. Vermesh, Q. Wang, Y. Li, and H. Dai, *Hysteresis caused by water molecules in carbon nanotube field-effect transistors*, Nano Lett. 3 (2003), pp. 193–198.
[9] R. Krupke, F. Hennrich, H. von Löhneysen, and M.M. Kappes, *Separation of metallic from semiconducting single-walled carbon nanotubes*, Science 301 (2003), pp. 344–347.
[10] J. Li, Q. Zhang, N. Peng, and Q. Zhu, *Manipulation of carbon nanotubes using AC dielectrophoresis*, Appl. Phys. Lett. 86 (2005), p. 153116.
[11] M. Washizu, S. Suzuki, O. Kurosawa, T. Nishizaka, and T. Shinohara, *Molecular dielectrophoresis of biopolymers*, IEEE Trans. Ind. Appl. 30 (1994), pp. 835–843.
[12] J. Zhao, A. Buldum, J. Han, and J.P. Lu, *Gas molecule adsorption in carbon nanotubes and nanotube bundles*, Nanotechnology 13 (2002), pp. 195–200.
[13] A. Bachtold, C. Strunk, J.P. Salvetat, J.M. Bonard, L. Forro, T. Nussbaumer, and C. Schonenberger, *Aharonov-Bohm oscillations in carbon nanotubes*, Nature 397 (1999), pp. 673–675.