

# Humidity Sensitivity of Carbon Nanotube and Poly (Dimethyldiallylammonium Chloride) Composite Films

Litao Liu, Xiongying Ye, *Member, IEEE*, Kang Wu, Zhaoying Zhou, Dongjin Lee, and Tianhong Cui, *Senior Member, IEEE*

**Abstract**—This paper demonstrates a highly sensitive humidity sensor based on carbon nanotube and poly (dimethyldiallylammonium chloride) composite films. The composite film is deposited between interdigitated electrodes on a Si/SiO<sub>2</sub> substrate through layer-by-layer self-assembly technique. The resistance stability of the composite film is effectively improved through thermal annealing, and I-V characteristic of the film exhibits a very good linear behavior. The resistance increases exponentially with relative humidity from 20% to 98%, and a much higher sensitivity in comparison with pure carbon nanotube networks is achieved. With temperature increased, the water vapor density versus RH shifts upwards, while the resistance is reduced downwards. The resistance is dependent on temperatures with a negative coefficient. The composite films with multiwalled carbon nanotubes show an adjacent sensitivity, compared with the single-walled carbon nanotube composite films. The experimental results show that the humidity sensors have a fast response and a short recovery time, and their response is reversible. A simple model is proposed to explain the change of composite film resistance with humidity. The carbon nanotubes junctions may play a more important role in the overall resistance change for water molecule absorption.

**Index Terms**—Carbon nanotube (CNT), composite film, humidity sensitivity, layer-by-layer (LbL) self-assembly, poly (dimethyldiallylammonium chloride).

## I. INTRODUCTION

CARBON NANOTUBES (CNTs) have attracted much attention due to their unique electrical, physical, mechanical, and chemical properties since the discovery of CNTs by Iijima in 1991 [1]. Researchers have been exploring the potential of CNTs in a wide variety of applications [2] including chemical and biological sensors [3], [4]. CNTs have been highly expected as a novel sensing material, since their hollow structure

with a very large surface area to volume ratio [5] is very suitable for physisorption or chemisorption with much more sensing targets. Some reports of gas sensing capabilities of carbon nanotubes through the charge transfer or capacitance change by gas adsorption (e.g., NH<sub>3</sub>, NO<sub>2</sub>, DMMP) [6]–[10] have shown the significant prospect of CNTs in sensing. Applications of CNTs as humidity sensors have also been reported [11], [12].

Recently, several research groups [13] are working on the functionalization of CNTs with different materials to enhance their sensing performance. There are two main approaches for the surface functionalization of CNTs: covalent functionalization and noncovalent functionalization, depending on the types of linkages of the functional entities onto CNTs. Functionalized CNT sensors often offer a higher sensitivity and a better selectivity, compared with the pristine CNT sensors. CNT/polymer nanocomposites as a noncovalent functionalization method without destruction of the physical properties of CNTs offer promising features as a sensing material. An *et al.* [14] fabricated single-walled carbon nanotube (SWNT) and polypyrrole (PPy) nanocomposite based gas sensors for NO<sub>2</sub> sensing. The sensor was formed by spin-coating nanocomposites onto prefabricated electrodes. The sensitivity of the nanocomposites was about ten times higher than that of polypyrrole. Abraham *et al.* [15] developed a wireless gas sensor using a multi-walled carbon nanotube (MWNT) and PMMA composite film. The sensor was fabricated by dip-coating the composite film on a pair of electrodes with interdigital fingers. The sensor shows a fast response and a large change of resistivity in an order of 10<sup>2</sup> – 10<sup>3</sup> for sensing dichloromethane, acetone, and chloroform.

In addition to spin-coating and dip-coating methods, layer-by-layer (LbL) self-assembly technique can be used to make CNT/polymer composite films. The LbL self-assembly technique is a unique method for the deposition of composite films with controllable thickness at a nanometer range, with the merits of low cost, and room temperature process, and high reproducibility and controllability. The LbL self-assembly technique has been investigated by several groups to deposit CNT thin films for various applications, such as ultrahard composite thin films [16], amperometric choline biosensors [17], semiconducting layer for field-effect transistor [18], etc. Recently, Yu *et al.* [19] fabricated composite multilayer films of oxidized MWNT and poly (ethyleneimine) (PEI) through the LbL self assembly approach and tested their humidity sensitive behaviors. The resistance of the multilayer films increases almost linearly with humidity in a range of 5%–85% RH. In

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L. Liu, X. Ye, K. Wu, and Z. Zhou are with the State Key Laboratory of Precision Measurement Technology and Instruments, Department of Precision Instruments and Mechanology, Tsinghua University, Beijing, 100084 China (e-mail: xyue@mail.tsinghua.edu.cn).

D. Lee and T. Cui are with Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455 USA (e-mail: tcui@me.umn.edu).

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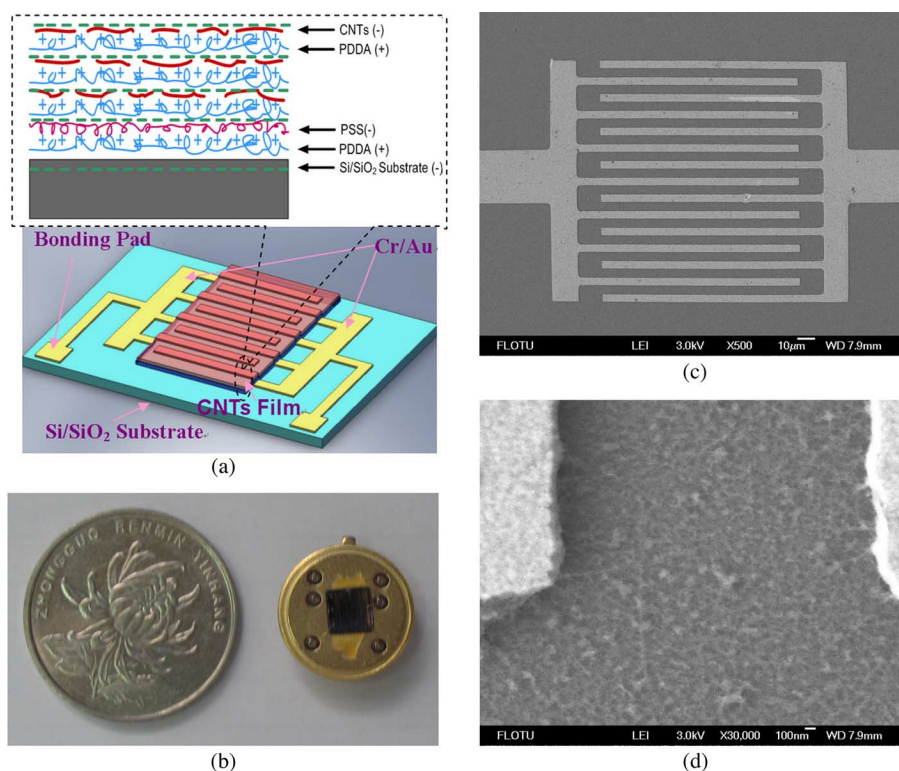


Fig. 1. (a) Structure of a CNT/PDDA composite film humidity sensor. An LbL-assembled CNT/PDDA composite film on Cr/Au IDE on a Si/SiO<sub>2</sub> substrate is as the sensing film. The LbL-assembled films consist of a (PDDA/PSS)<sub>2</sub> precursor film and a (PDDA/CNT)<sub>n</sub> film. (b) Optical image of a fabricated sensor. (c) SEM of an IDE with CNT/PDDA composite film. (d) SEM of an assembled CNT/PDDA composite film.

our previous study, a high-performance ACh sensor based on the LbL self-assembled SWNT conducting film and AChE sensing film was fabricated [20], and we also investigated humidity sensitivity of pure MWNT networks deposited by dielectrophoresis [21]. In this paper, we present humidity sensors utilizing a carbon nanotube and poly (dimethyldiallylammonium chloride) (PDDA) composite film. The CNT/PDDA composite film with multilayers is deposited on interdigitated electrodes (IDEs) with the LbL self-assembly technique. The resistance of CNT/PDDA composite films becomes stable after several times of thermal annealing. The humidity sensing principle is based on the change in the resistance of the CNT/PDDA film due to the presence of water vapors. The humidity sensitive behavior of the CNT/PDDA films is investigated.

## II. EXPERIMENTAL

### A. Preparation

MWNTs and SWNTs produced by chemical vapor deposition (CVD) from Chengdu Organic Chemical Compant, Ltd., were used in our experiments. The MWNTs were 10–20 nm in diameter and 20 μm in length with a purity of 95%. The SWNTs were 1–2 nm in diameter and 50 μm long and the purity was 90%. In order to functionalize the CNTs and remove residual catalysts and amorphous carbon particles in the meantime, the raw CNTs were treated with concentrated nitric and sulfuric acids (1 : 3 HNO<sub>3</sub> : H<sub>2</sub>SO<sub>4</sub>) at 110°C for 45 min. The acid treatment can greatly enhance the solubility of CNTs to water by introducing hydrophilic carboxylic (–COOH) functional groups to the sidewalls and ends of CNTs [22]. The functionalized CNTs

with negative charges were dispersed uniformly in deionized water with a concentration of approximately 1 mg/ml through ultrasonic vibration.

Aqueous polyelectrolyte solutions were obtained from Sigma-Aldrich and diluted with deionized water. The concentrations of PDDA (polycation, molecular weight of 200 000–350 000) and PSS (polyanion, molecular weight of 70 000) are 15 and 3 mg/ml, respectively. NaCl (0.5 M) was added to both solutions to increase the ionic strength of the polyelectrolytes. The two polyelectrolytes were used as the electrostatic “glue” in the LbL self-assembly process to form stable and strong multilayer films. More details in material preparation can be found in our previous report [23].

### B. Fabrication

Fig. 1(a) shows the structure of a humidity sensor and the construction of a CNT/PDDA multilayer composite film as the sensing material. The humidity sensor was built on a silicon wafer with a layer of SiO<sub>2</sub> 200 nm thick. Chromium (Cr, 40 nm) and gold (Au, 300 nm) layers were deposited by sputtering and patterned by photolithography and etching to form IDEs, the fingers of the IDEs are 8 μm wide and 120 μm long with a gap of 8 μm. The composite film was deposited on the substrate with LbL self-assembly process. First, the wafer was alternately immersed in aqueous PDDA and PSS solutions, in a sequence of [PDDA(10 min) + PSS(10 min)]<sub>2</sub>. These two (PDDA/PSS) bilayers served as precursor layers to enhance the subsequent adsorption of CNTs. Following the precursor multilayer, some CNTs layers are coated on the substrate alternately with PDDA. The sequence of the alternate immersion is

[PDDA(10 min) + CNT(15 min)]<sub>n</sub>, where *n* represents the number of (PDDA/SWNT) bi-layers. The dipping times used for polyelectrolytes and CNTs were 10 and 15 min, respectively. Intermediate rinsing with DI water and drying with a nitrogen flow are required to remove the excessive polyelectrolytes and CNTs. The above cycle was repeated until the desirable cycles or layers were obtained.

Fig. 1(b) shows an optical image of a fabricated humidity sensor on a chip of 5 mm × 5 mm. A scanning electron microscope (SEM) image of an IDE with SWNT/PDDA composite film and a magnification of a SWNT/PPDA composite film are shown in Figs. 1(c) and 1(d), respectively. The SWNTs form a dense network. The average thickness of a PDDA layer and an SWNT layer are approximately 2.8 nm and 4.8 nm, respectively [24]. The thickness of the SWNT layer is approximately equal to the diameter of the SWNT bundles, therefore the rough thickness of an MWNT layer should be equal about to the mean diameter of the MWNTs (15 nm). Four types of humidity sensors with different CNT/PPDA composite films were used in this study including SWNT and MWNT with 5 and 8 layers, respectively. The effective thicknesses of the SWNT/PDDA with 5 and 8 layers were about 38 and 61 nm, respectively. The thicknesses of the MWNT/PDDA with five and eight layers should be about 90 and 145 nm, respectively.

### C. Measurement

Before the testing of humidity sensing behaviors, the sensors were put into a furnace under atmosphere for repeated thermal annealing to improve their stability. The furnace was heated up to 80 °C from room temperature within 10 min, and the temperature was kept for 30 min followed by cooling down naturally. The above thermal annealing was repeated until the resistance of the sensors remained almost unchanged at room temperature. Humidity testing experiments were conducted by exposing the sensors to different relative humidity using a High-Low Temperature and Humidity Chamber (PHC1002-M, Wuxi Partner Science & Technology Company, Ltd., China). The chamber cubage is 225 L, and the control accuracy of temperature and humidity are ±2.0 °C and ±3.0% RH, respectively. In the static testing experiments, the sensors are exposed in the chamber with a desired humidity and temperature until the output signals get steady. The RH range is controlled from 20% to 98% at a fixed temperature. The temperature dependence of resistance was measured at the same RH. In the dynamic test, the sensors are alternately exposed at 25% and 75% RH by putting them in the humidity chamber (25% RH), and taking out to atmosphere (75% RH) at room temperature. We defined the response time and recovery time when the sensor achieved 90% of the total resistance variation when RH increases and decreases. The electrical measurement was performed using a Keithley 237 source-measure unit through the computer-controlled LabVIEW program.

## III. RESULTS AND DISCUSSION

Thermal annealing is an important process for the stabilization of carbon nanotube and polymer composite. Fig. 2 shows the resistance of a typical five-layer SWNT/PDDA composite film measured at room temperature after each annealing cycle. The resistance became smaller and stable after six annealing

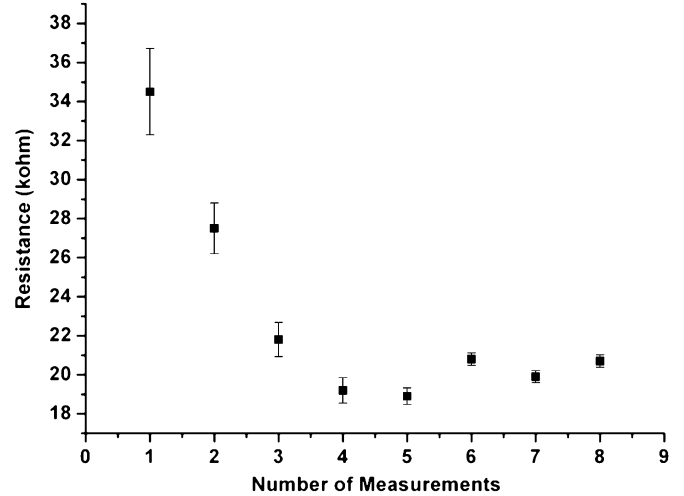


Fig. 2. Resistance of a typical five-layer SWNT/PDDA composite film with respect to repeated thermal cycles measured at 25 °C.

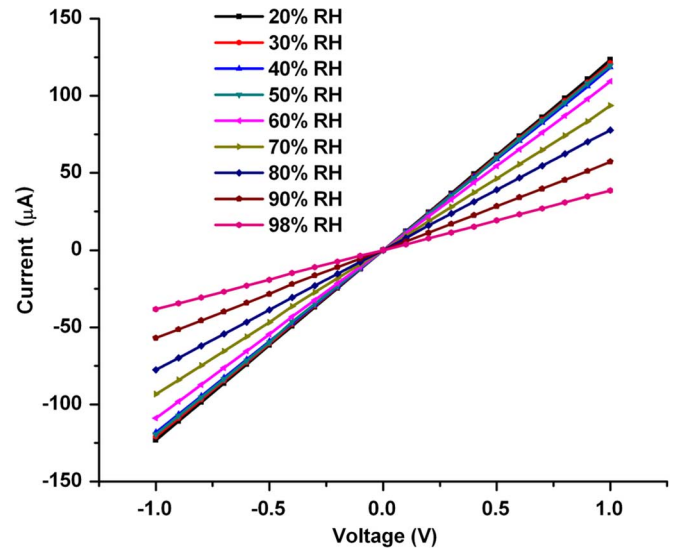


Fig. 3. I-V curves of a typical eight-layer SWNT/PDDA sensor at different RH from 20% to 98%, measured at 25 °C.

cycles. It was also found that several thermal annealing cycles were very necessary to stabilize the resistance of the MWNT/PDDA composite films.

Fig. 3 shows the I-V curves of a typical eight-layer SWNT/PDDA composite film at different RH from 20% to 98% at 25 °C. In any RH atmosphere, the I-V curves of the sensor exhibit a very good linearity, and other sensors show the same behavior. In the meantime, it is clearly seen that the resistance of the composite film decreases promptly with the increase of RH.

The resistances of four sensors (5, 8-layer MWNT/PDDA and 5, 8-layer SWNT/PDDA) were measured at different RH from 20% to 98%. The sensitivity of the sensors can be defined as

$$S = \Delta R/R_{20} \times 100\% = \frac{R_{RH} - R_{20}}{R_{20}} \times 100\% \quad (1)$$

where  $R_{RH}$  is the steady-state resistance after exposure to selected RH, and  $R_{20}$  is the resistance measured at RH of 20%.

For the given humidity range, the resistances of the sensors based on the CNT/PDDA composite films increased with RH,

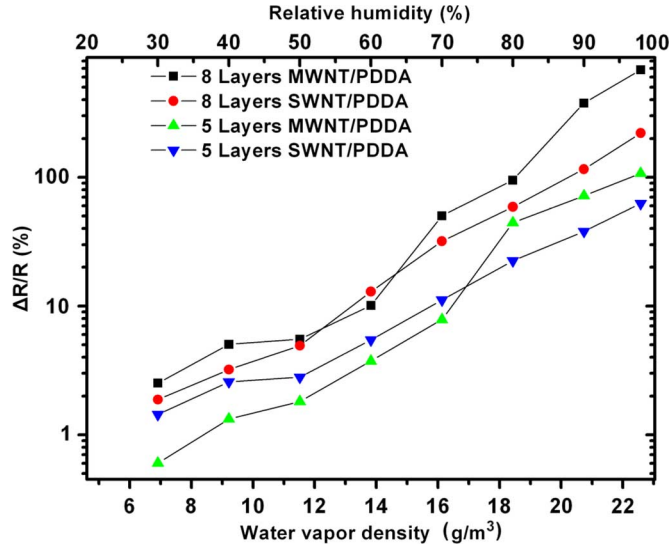


Fig. 4. Sensitivity of the sensors with different CNT/PDDA composite films measured at 25 °C, the resistance at RH of 20% is set as the reference.

which exhibited a linear response to RH, that is the water vapor density change in semi-logarithmic scale, as shown in Fig. 4. The water vapor density is obtained by multiplying the relative humidity with the saturated water vapor density at the fixed temperature. Among the four humidity sensors, the experimental results suggest that CNT/PDDA composite films with eight layers seem slightly more sensitive than that with five layers for humidity sensing. Further experiments are needed to gain more understanding of the effect of the layer number on the sensitivity. The type of carbon nanotubes did not markedly affect the humidity sensitivity of the composite films. The composite films with MWNTs show a little higher sensitivity in the higher RH range (higher than 80%) in comparison with SWNTs, while in the lower RH range, the sensitivities did not show a clear difference.

In this research, we establish a model to explain and analyze the change of composite film resistance with humidity. The current distribution can be assumed to be uniform when the thickness of a sensing film is much smaller than the gap between two electrodes, as indicated in Fig. 5(a). The PDDA layers can be considered as the insulating layers between the CNT conductive layers, therefore the overall resistance of the CNT/PDDA composite film can be considered as the sum of  $n$  layer resistances,  $R$ , in parallel, and each  $R$  is composed of  $m_1$  site resistances of CNTs and  $m_2$  site resistances of CNT junctions in series, as shown in Fig. 5(b). When the film adsorbed water, the layer resistance,  $R$ , can be expressed as

$$R = (m_1 \times r'_{NT} + m_2 \times r'_J) \times \theta + (m_1 \times r_{NT} + m_2 \times r_J) \times (1 - \theta) \quad (2)$$

where  $m_1$  and  $m_2$  are the number of active site resistance of CNTs and CNT junctions in one layer,  $r_{NT}$  and  $r_J$  are the vacant site resistance of CNTs and CNT junctions,  $r'_{NT}$  and  $r'_J$  are the occupied site resistance of CNTs and CNT junctions, and  $\theta$  is the fraction of site coverage of adsorption, respectively. We assume that  $\theta$  is equal every layer when considering the static testing.

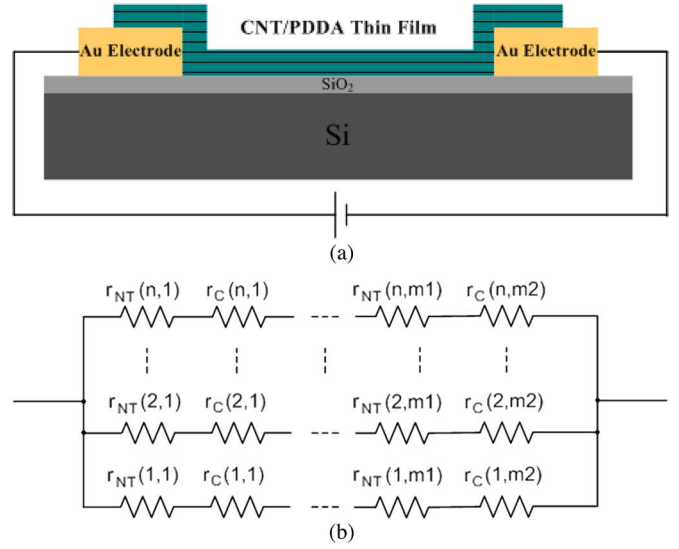


Fig. 5. (a) Device configuration and (b) circuit model of a CNT/PDDA composite film.

The change of the resistance depends on the interaction of water molecules with the CNT sites and CNT junction sites. The reason why resistance increases with RH mainly includes: the increase of tunneling barriers between the CNT junctions due to the introduction of the water molecules, the swelling of the polymer due to absorption of water molecules, and the charge transfer when water molecules are adsorbed on CNT surfaces. The increase of tunneling barriers directly leads to the resistance of CNT junctions increasing [29]. The swelling of the polymer effectively increases the contact gap of the CNT intertube junctions in the composite film, which also increases the CNT junction resistance [26]. Water molecules can be adsorbed on the surfaces of CNTs by physisorption, and there is a charge transfer from water molecules to CNTs, also resulting in an increase in resistance [25]. If the gap size between electrodes is very large compared to the length of the CNTs, the CNT junction resistances dominate in the CNT films [27]–[29], therefore the junctions may play more important role in resistance change for water molecules absorption. Thus the MWNT/PDDA composite films show an adjacent sensitivity with the SWNT/PDDA composite films for sensing humidity. Though semiconducting CNTs exhibit much a larger response than metallic CNTs when exposed to gas environment [30], MWNTs can adsorb more gases as MWNTs have more defects than SWNTs [31], [32]. This may result in MWNT/PDDA having better sensitivity than SWNT/PDDA at a higher RH range.

According to the Park model [33], [34], the amount of water molecules absorbed by the film at our measured range corresponds the dual mode Henry-Clustering model (HC). This model consists of two parts: Henry's law, and water clustering. The fraction of site coverage of adsorption  $\theta$  can be expressed as

$$\theta = k_H a_w + K_a a_w^n \quad (3)$$

where  $k_H$  is the Henry's solubility coefficient,  $K_a$  is the Equilibrium constant for the clustering reaction,  $n$  is the mean number of water molecules per cluster, and  $a_w$  is the water

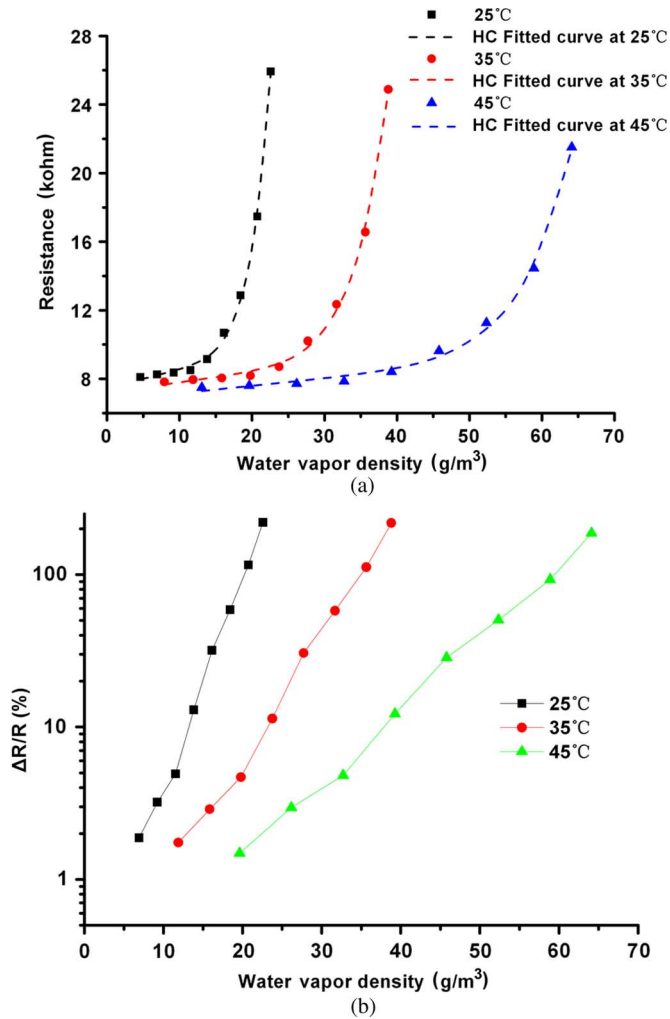


Fig. 6. Resistance-humidity relationship of the eight-layer SWNT/PDDA sensor at a different temperature. (a) Resistance versus water vapor density, the dashed lines were fitted using HC model. (b) Sensitivity versus water vapor density.

vapor density, respectively. Therefore, the resistance can be derived from (2) and (3), and is given by

$$R = A + B(k_H a_w + K_a a_w^n) \quad (4)$$

where

$$A = m_1 \times r_{NT} + m_2 \times r_C,$$

$$B = m_1 \times (r'_{NT} - r_{NT}) + m_2 \times (r'_C - r_C).$$

The temperature influence on the humidity sensing behavior was tested. Fig. 6 presents the relationship between water vapor density and the resistance of the eight-layer SWNT/PDDA sensor in the range 25 °C–45 °C. Fig. 6(a) shows the resistance change with the water vapor density at different temperatures. The points in the figure are the experimental test data, and the dashed lines in the figure are the fitted curves of the resistances to the HC model. The experimental data are very well fitted by the HC model. Fig. 6(b) shows the sensitivity with the water vapor density at different temperatures. The sensitivities are all linear to the water vapor density change in semi-logarithmic scale. With the same water vapor density, the resistance is lower at higher temperature. The resistances of the CNT/PDDA

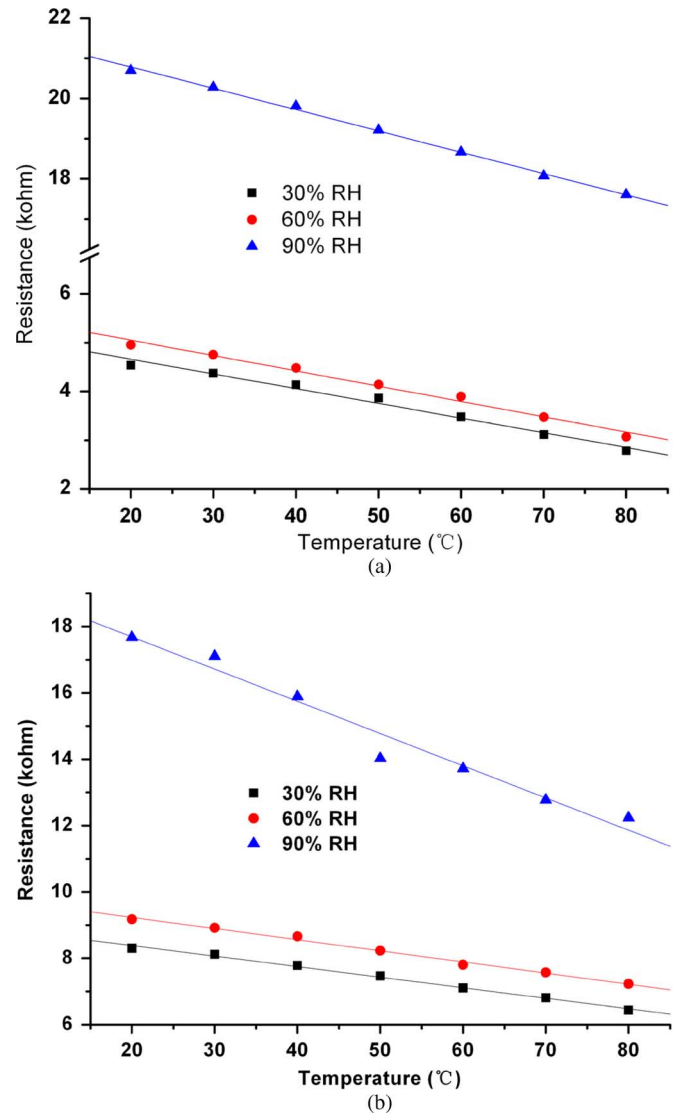


Fig. 7. Resistance-temperature relationship of (a) the eight-layer MWNT/PDDA sensor and (b) the eight-layer SWNT/PDDA sensor at a fixed RH.

sensors at a larger temperature range were measured at three fixed RH: 30%, 60%, and 90%. The resistance-temperature relationship of the eight-layer MWNT/PDDA and eight-layer SWNT/PDDA sensors were shown in Fig. 7. The resistance linearly decreased with a negative temperature coefficient. The nonmetallic temperature dependence of the conductivity also indicates the presence of tunneling barriers, which may dominate the overall film resistance. Though the tunneling barriers between CNT junctions increase with more water molecule adsorbed at a higher water vapor density, more charge carriers can transport through the barriers at high temperatures. Furthermore, both the Henry's solubility coefficient,  $k_H$ , and the Equilibrium constant for the clustering reaction,  $K_a$ , would reduce with the temperature increase. Therefore, the overall film resistance reduces with temperature increase at the same water vapor density. The experimental results also present that the film resistance reduces with temperature increase at the same RH. We may conclude that the temperature affect on resistance change is larger than the RH at the experimental temperature range.

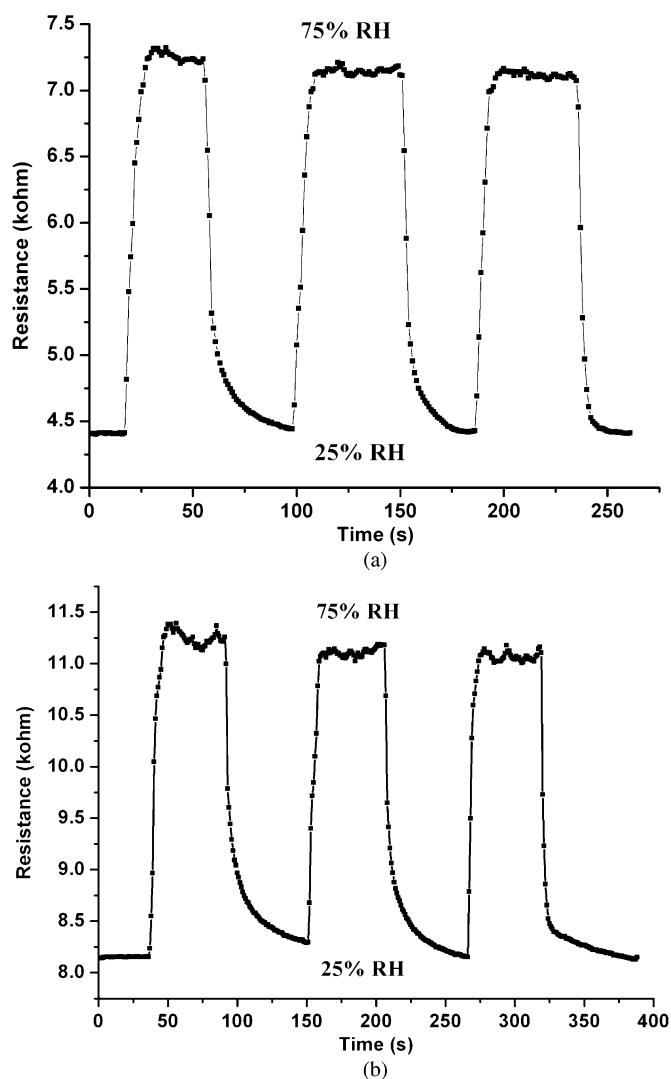


Fig. 8. Typical response and recovery curve of (a) the eight-layer MWNT/PDDA sensor and (b) the eight-layer SWNT/PDDA sensor.

Fig. 8 illustrates a time response and recovery curve of the eight-layer MWNT/PDDA sensor and the eight-layer SWNT/PDDA sensor alternately exposed at 25% and 75% RH. It is estimated that the response time of the eight-layer MWNT/PDDA sensor is about 8 s, and the recovery time is about 35 s. For the eight-layer SWNT/PDDA sensor, the response time and the recovery time are 8 s and 40 s, respectively. It is evident that changes in the film resistance with RH are reversible at room temperature. The CNT/PDDA composite films exhibit a higher sensitivity to humidity, especially at high relative humidity, in comparison with pure MWNT networks, and the sensors with the composite films have a good repeatability, better than the pure CNT network sensors [21].

#### IV. CONCLUSION

In conclusion, we have fabricated a new humidity sensor based on LbL self-assembled CNT/PDDA composite films. The LbL nano self-assembly process provides an easy and effective method to deposit and control the MWNT or SWNT and PDDA composite film thickness. The resistance stability

of CNT/PDDA composite films was effectively improved through thermal annealing. The resistances of CNT/PDDA composite films increase exponentially with an increase in humidity. The experiment results suggest that the self-assembled MWNT/PDDA composite films have an adjacent sensitivity for humidity sensing with the SWNT/PDDA films. The CNT junction resistance may dominate the humidity sensing in the CNT/PDDA composite films. The temperature effect of the CNT/PDDA films on resistance changes cannot be neglected. The sensors show a high sensitivity, a fast response, and a good reversibility.

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**Litao Liu** received the B.S. degree in precision instruments and mechanism from Tsinghua University, Beijing, China, in 2004. He is currently working towards the Ph.D. degree in instrument science and technology at Tsinghua University.

His main research includes work in the micro/nano manufacturing; nanomaterial based chemical and biological sensors.

**Xiongying Ye** (M'06) received the B.S. and M.S. degrees from Shinshu University, Japan, in 1984 and 1986, and the Ph.D. degree from the University of Tokyo, Tokyo, Japan in 1989.

She is currently a Professor at the Department of Precision Instruments and Mechanology and the Micro/Nano Technology Research Center, Tsinghua University. She is a member of the standing council of the Chinese Society of Micro-Nano Technology and a member of the standing council of the MEMS&NEMS of Society China, CIS. Her current research interests include micro/nano sensors, micro fluidics; polymer MEMS process, etc.

**Kang Wu** received the B.S. and M.S. degrees in fluid mechanics at the Beijing University of Aeronautics and Astronautics, Beijing, China, in 2003 and 2005, respectively. He is currently working towards the Ph.D. degree in instrument science and technology at Tsinghua University, Beijing.

His research interests are microelectromechanical systems (MEMS) and microfluid mechanics.

**Zhaoying Zhou** received the B.S. degree from the Department of Precision Instruments, Tsinghua University, Beijing, China, in 1961.

He is a Professor at the Department of Precision Instruments and Mechanology, Tsinghua University. From 1979 to 1981, he was a Visiting Scientist in the Department of Automatic Control, Lund University, Sweden. Since 1987, he has been a Professor at the MEMS Laboratory, Precision Instruments and Mechanology Department, Tsinghua University. He is an Editor of the *International Journal of Micromechanics*. His recent research interest is in the fields of measurement, control and Micro/Nano technology.

Prof. Zhou is the Vice President of China Instrument Society, the Honor Vice President of China Micro/Nano Technology.

**Dongjin Lee** received the B.S. and M.S. degrees in mechanical engineering from Korea University, Seoul, Korea, in 2003 and 2005, respectively. He is currently working towards the Ph.D. degree at the Department of Mechanical Engineering, University of Minnesota, Minneapolis.

His main research topics include micro/nano manufacturing, nanomaterial-based sensors and actuators, chemical and biological sensors, micro and nanoelectromechanical systems (M/NEMS), and general nanotechnology.

**Tianhong Cui** (SM'04) received the B.S. degree from the Nanjing University of Aeronautics and Astronautics, Nanjing, China, in 1991, and the Ph.D. degree from the Chinese Academy of Sciences, Beijing, in 1995.

He is currently a Nelson Associate Professor of Mechanical Engineering at the University of Minnesota, Minneapolis. From 1999 to 2003, he was an Assistant Professor of Electrical Engineering at Louisiana Technical University. Prior to that, he was a STA Fellow at the National Laboratory of Metrology, and served as a Postdoctoral Research Associate at the University of Minnesota and Tsinghua University. His current research interests include MEMS/NEMS, nanotechnology, and polymer electronics.

Prof. Cui is a member of the American Society of Mechanical Engineers (ASME).