Novel capacitance-type humidity sensor based on multi-wall carbon nanotube/SiO$_2$ composite films

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Abstract: A novel capacitance-type relative humidity (RH) sensor based on multi-wall carbon nanotube/SiO$_2$ (MWCNTs/SiO$_2$) composite film is reported. Details of the fabrication process, possible sensing mechanism and sensing characteristics, such as linearity and sensitivity, are described. The capacitance of the MWCNTs/SiO$_2$ composite film shows typical concentration percolation behavior with increasing MWCNT loading. At loadings below the percolation threshold (1.842wt%), the sensor capacitance increases obviously with increasing MWCNTs. The water condensed in the MWCNTs/SiO$_2$ layer can lower the percolation threshold and increase the sensor capacitance. The sensor with MWCNT concentration of 1wt% has the best properties. The sensor has a humidity sensitivity of about 673 pF/% RH and a linearity correlation of 0.98428. The response time of the sensor to RH is about 40 s and the recovery time is about 2 s.

Key words: carbon nanotubes; humidity sensor; percolation threshold; capacitance-type
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1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention since their discovery by Iijima in 1991[1] due to their potential applications in the fields of novel sensors[2–5], hydrogen storage materials[6,7], field-effect transistors[8–10] and field emission displays[11–13]. There have been high expectations for CNTs as novel sensing materials, since their hollow cores with large surface area are well suited to physisorption and chemisorption, and CNT-based gas sensors with high sensitivity and a high response speed have been demonstrated for detecting humidity[14,15]. However, the capacitance-type humidity sensor based on multi-wall carbon nanotubes is nonlinear to the increment of RH[4,16].

To overcome these drawbacks of MWCNT-based humidity sensors, we have developed a novel capacitance-type humidity sensor based on multi-wall carbon nanotube/SiO$_2$ composite film. This device shows good linearity of capacitance over a wide humidity range. To enhance the sensitivity of the sensor, a MWCNT concentration of about 1wt% was chosen. The humidity sensitivity properties were investigated and possible sensing mechanisms were discussed.

2. Experimental details

The sensor (in Fig. 1) consists of a pair of Al interdigital electrodes and a multi-wall carbon nanotube (MWCNT) film coated on the Al electrodes. An Al film with a thickness of 1 μm was first evaporated on the glass substrate, and then patterned into interdigital electrodes by photolithography.

The CNTs were functionalized by HNO$_3$ at 140 °C for 4 h to make them suspended with -OH and -COOH groups, which can make the CNTs hydrophilic. After that, the layer of MWCNT/SiO$_2$ composite was coated on the Al electrodes by the technique of silk screen printing. All of the chemicals used in the work were of analytical grade.

A series of humidity environments were achieved by encapsulating saturated aqueous solutions of LiCl, MgCl$_2$, K$_2$CO$_3$, Mg(NO$_3$)$_2$, CuCl$_2$, NaCl, KCl and K$_2$SO$_4$ in glass vessels at room temperature, which yielded sealed atmospheres with relative humidity (RH) of 11%, 33%, 43%, 52%, 67%, 75%, 86% and 97%, respectively[4]. The capacitance of the structures was measured using an LCR meter-PM6306 (5 kHz test signal) in the glass vessels at room temperature throughout the testing.

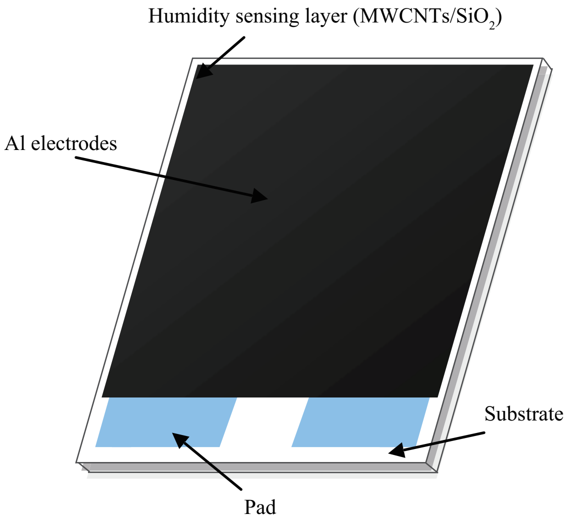

Fig. 1. Schematic diagram of the sensor.

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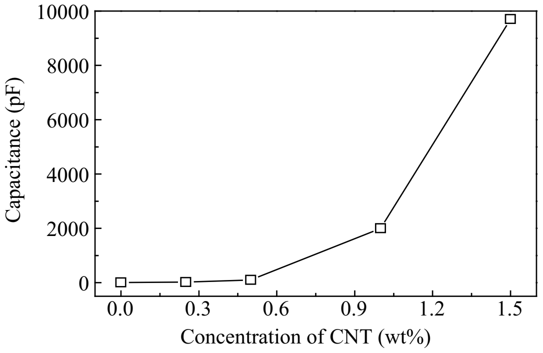

Fig. 2. Capacitance of the sensor as a function of MWCNT concentration.

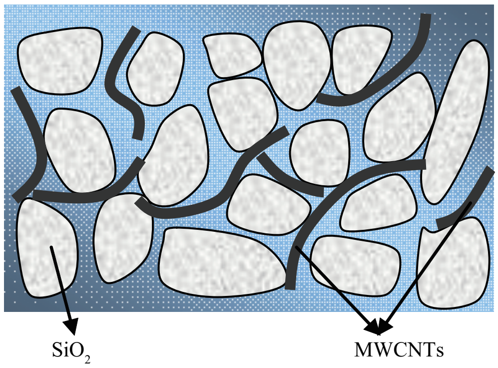

Fig. 3. Sketch map of the structure in MWCNTs/SiO_2 films.

3. Results and discussion

3.1. Capacitance of the sensor

In order to discuss the sensor capacitance dependence on the MWCNT concentration, five sensors were fabricated with MWCNT concentrations of 0wt%, 0.25wt%, 0.5wt%, 1wt% and 1.5wt%. Figure 2 shows the capacitance of the sensor as a function of the MWCNT concentration. The capacitance of the pristine SiO_2 sensor was about 7.3 pF. For low MWCNT concentrations (from 0wt% to 0.5wt%), the sensor capacitance was essentially equal to that of the pristine SiO_2 sensor.

The sharp increase in capacitance value was observed between 0.5wt% and 1.5wt%, where the capacitance changed from 97.4 to 9699 pF. This behavior has been attributed to the occurrence of a percolation transition[17,18]. The MWCNTs/SiO_2 films can be assumed as a three-dimensional (3D) granular composites consisting of MWCNT molecules randomly dispersed in non-conducting SiO_2, as shown in Fig. 3. In the percolation model, the capacitance remains a stable value to a certain weight fraction of the CNTs. However, as the content of CNTs reaches a critical concentration or percolation threshold, some CNTs begin to get closer to each other and the distance between them decreases, which gives rise to the capacitance of the sensor.

To estimate the percolation threshold more precisely, the experimental data were fitted to the scaling law of percolation theory[19],

$$C = C_1(f_C - f)^{-s}, \quad f < f_C, \qquad (1)$$

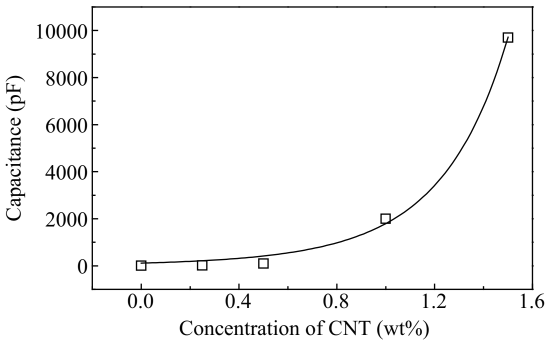

Fig. 4. Fitting curve of the sensor capacitance to different MWCNT concentrations.

Table 1. Parameter values in Eq. (1) from fitting the experimental data.

Parameter	Value
C_1	0.08728 pF
f_C	1.842%
s	2.04673
R^2	0.988

where C is the capacitance of the sensor, C_1 is proportional coefficient, f is the weight concentration of the MWCNTs, f_C is the percolation threshold, and s is the critical exponent. Equation (1) is valid when $f < f_C$. The fitting curve to Eq. (1) is shown in Fig. 4. This fit is determined by the variable (f_C, C_1 and s) until the best fit to the equation is found. The best fit of the capacitance data results in $f_C = 1.842$wt% (shown in Table 1).

The values of the percolation threshold (1.842wt%) are in reasonable agreement with the result in Ref. [18]. In Ref. [18], the percolation threshold is about 0.9wt%, which is about a half of that in our work. The difference in percolation threshold might be caused by the different dimension of the MWCNTs. In Ref. [18], the length of the MWCNT is 5–15 μm, but in our work the MWCNT length is about 1–2 μm. When the MWCNTs are longer, it will be easy for them to contact each other and to form a conductive path in the composite, thus the percolation threshold will be lower.

3.2. Response of the sensor to humidity

The dependence of the sensor response to humidity on the MWCNT concentration is measured at relative humidity (RH) from 11% to 97%. Figure 5 shows the sensor capacitance as a function of RH for samples with different MWCNT concentrations. The ordinate of the figures is the relative variation in capacitance ($\Delta C/C$), where ΔC is the variation in capacitance and C is the static value of the capacitance.

The MWCNTs and SiO_2 form porous nano-structures in the MWCNT–SiO_2 layer because of their random entanglement and alignment, as shown in Fig. 6.

Due to the existence of these capillary pores, fewer vapor molecules from a lower RH level are required to induce vapor condensing into water in these pores. Because the MWCNTs have a much higher surface area, vapor molecules can be adsorbed onto the MWCNT surface, which can also cause capillary condensation. Therefore, condensation can occur in these

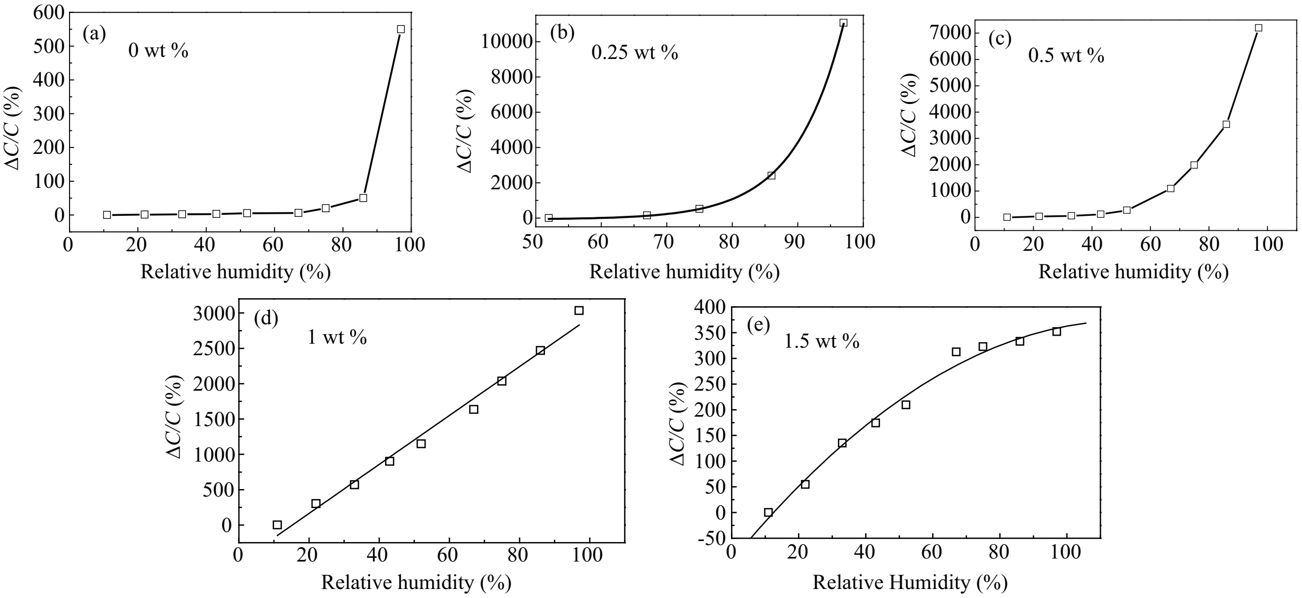

Fig. 5. Humidity dependence of the capacitance of the sensors with different MWCNT concentrations.

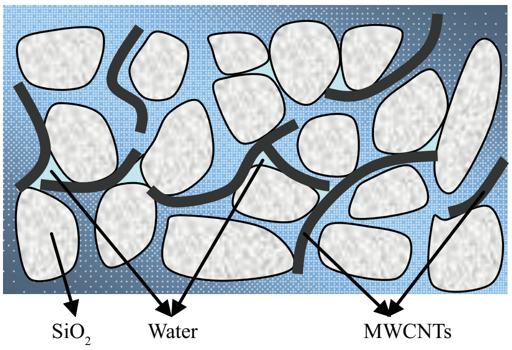

Fig. 6. Diagram of the water condensation in MWCNT/SiO$_2$ films.

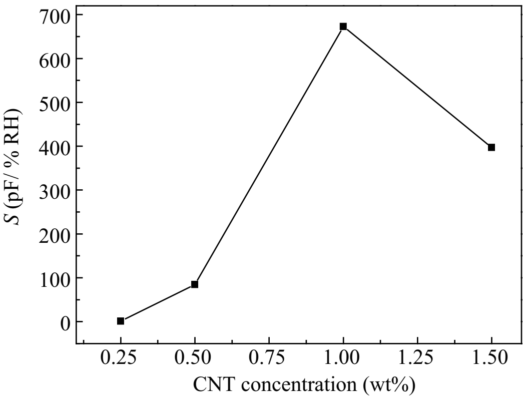

Fig. 7. Capacitance sensitivity of the sensors as a function of MWCNT concentration.

capillary pores earlier at lower RH level than under the normal saturated vapor pressure at higher RH or even 100%RH[20]. The water condensed in the MWCNTs/SiO$_2$ layer can also contact the MWCNTs to form conductive paths in the sensing film, which can make the percolation threshold lower. According to Eq. (1), when the percolation threshold f_C is low, the capacitance of the sensor will increase obviously. This increase in the capacitance can cause the sensor to be sensitive to the RH.

Shown in Fig. 5, curve a for a pure SiO$_2$ film sensor is highly nonlinear to the RH increment. In comparison with a pure SiO$_2$ sensor, curves b, c, d and e with MWCNT concentrations of 0.25wt%, 0.5wt%, 1wt% and 1.5wt% were obtained. The sensor with an MWCNT concentration of 1wt% has the best linearity, and the linearity correlation (R^2) is 0.98428.

As the static capacitance (C) of the sensor becomes obviously large with the increment of MWCNT concentration, the relative variation in capacitance ($\Delta C/C$) will decrease. For assessing the capacitance response of the sensor to RH with different MWCNT concentrations, the sensor sensitivity (S) is defined as

$$S = \frac{C_{97\%} - C_{11\%}}{97\%\mathrm{RH} - 11\%\mathrm{RH}}, \tag{2}$$

where $C_{97\%}$ and $C_{11\%}$ represent the capacitance of the sensors measured at RH = 97% and RH = 11%, respectively. By the testing datum and Eq. (2), when the MWCNT concentration is 1wt%, the sensitivity (S) of the sensors reaches its maximum (673 pF/%RH) as shown in Fig. 7.

3.3. Response and recovery characteristics

The response and recovery behavior, corresponding to the water molecule adsorption and desorption process, is an important characteristic for evaluating the performance of humidity sensors. The response and recovery processes of the sensor can be seen in the test, and this experiment is operated between 11% RH and 97% RH. The sensor with 1wt% MWCNTs has been chosen in this experiment as it has the best linearity and highest sensitivity. The response speed of the sensor to humidity is reflected in the response time, which is defined as the time that took by the sensor as the output changes from the initial value to 90% of the final value when the RH springs from one value to another.

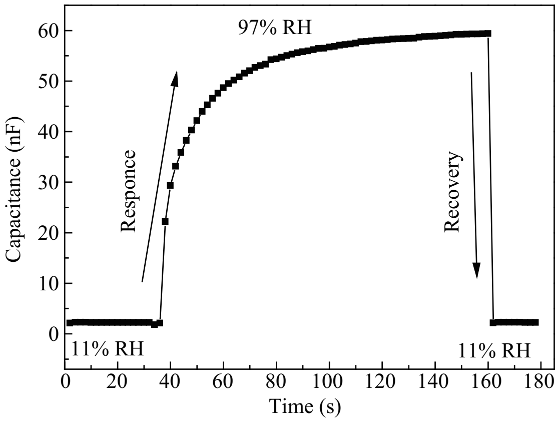

Fig. 8. Adsorption and desorption procedure of the sensor.

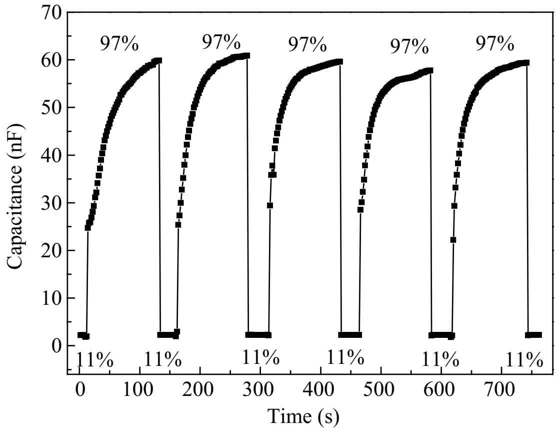

Fig. 9. Repeatable responses of the sensor during five cycles between 11% and 97% RH.

The response time is about 40 s and the recovery time is about 2 s, according to the process of adsorption and desorption shown in Fig. 8. The time of the adsorption process is longer than that of the desorption process, which means that capillary condensation will cost more time than evaporation of the water in dry circumstances.

3.4. Repeatable response and regeneration of the sensor

The performance of any commercially viable sensor has to be repeatable. Figure 9 shows reversible changes in the sensor capacitance as the relative humidity is varied cyclically. The experiment is repeated at room temperature at two relative humidity points, 11% (RH) and 97% (RH), and the sensor will stay 2 min in 97% (RH) and 0.5 min in 11% (RH), respectively. The maximum of the capacitance variations in each cycle is 57.62 nF, 58.66 nF, 57.38 nF, 55.52 nF and 57.16 nF, respectively.

4. Conclusion

A kind of humidity sensor based on MWCNT/SiO_2 has been fabricated. The capacitance properties of sensors with different MWCNT concentrations have been measured at room temperature. The experimental results showed that the sensor capacitance increased with MWCNTsconcentration. Porous nano-structures formed in the MWCNTs/SiO_2 layer can make the water vapor condense at a lower RH level, and water condensed in the MWCNT/SiO_2 layer can make the percolation threshold lower and increase the sensor capacitance. The sensor with a MWCNT concentration of 1wt% has the highest sensitivity and best linearity in our experiment. The sensor sensitivity is about 673 pF/% RH and the linearity correlation is 0.98428. These results demonstrate great potential for the practical realization of humidity sensors capable of working over a wide range of humidity with good sensitivity and linearity.

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