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Sensing Properties of a Novel Temperature Sensor Based on Field Assisted Thermal Emission

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Abstract: The existing temperature sensors using carbon nanotubes (CNTs) are limited by low sensitivity, complicated processes, or dependence on microscopy to observe the experimental results. Here we report the fabrication and successful testing of an ionization temperature sensor featuring non-self-sustaining discharge. The sharp tips of nanotubes generate high electric fields at relatively low voltages, lowering the work function of electrons emitted by CNTs, and thereby enabling the safe operation of such sensors. Due to the temperature effect on the electron emission of CNTs, the collecting current exhibited an exponential increase with temperature rising from 20 °C to 100 °C. Additionally, a higher temperature coefficient of 0.04 K^{-1} was obtained at 24 V voltage applied on the extracting electrode, higher than the values of other reported CNT-based temperature sensors. The triple-electrode ionization temperature sensor is easy to fabricate and converts the temperature change directly into an electrical signal. It shows a high temperature coefficient and good application potential.

Keywords: temperature sensor; carbon nanotubes; ionization; emission

1. Introduction

Temperature sensors are among the most-widely used sensors in consumer and industrial temperature measurement. The development goal of a temperature sensor usually includes high sensitivity, small footprint, and low power consumption. The potential of a carbon nanotubes (CNTs) based temperature sensor offers great opportunities towards extreme miniaturization and low power consumption [1–5], thanks to the unique nanoscale structure and electrical property [6–11]. Recent studies showed that CNTs could be used to construct temperature sensors. For example, a thermometer can be realized by measuring the thermal expansion of gallium inside a CNT [1], since the height of a continuous unidimensional column of liquid gallium inside a carbon nanotube varies linearly and reproducibly in the temperature range 50–500 °C. Nevertheless, this methodology requires microscopic measurement of the height of the gallium. Alternatively, the CNT-based temperature sensors [2–5] can also be implemented by measuring the conductivity variation of CNT induced by the thermal interaction. However, the application of this type of sensor is potentially limited by its complex fabrication process and low sensitivity. A novel ionization temperature sensor based on CNTs electrodes [12] was capable of overcoming the limitations of the above two types of temperature sensors, but it was only used to detect temperature in N_2 at 100 V extracting voltage; meanwhile, its carbon nanotubes have large diameter and small spaces between nanotubes (see supplementary material Figure S1), which results in small field enhancement factor, small output current, and low sensitivity—especially below 70 °C (see supplementary material Tables S1 and S2, Figure S2). In this paper, a triple-electrode CNT-based ionization temperature sensor is fabricated. Differently, the CNTs array is grown by a low-temperature thermal chemical vapor deposition (TCVD) process, enabling small diameters and larger spaces between nanotubes. As a result, the electric field around CNT tips and the emission current density of the tips can be enhanced [13]. In addition, the decrease of the electrode separation can increase the electric field strength of the sensor. The fabricated CNT temperature sensor is capable of detecting temperature in ambient atmosphere at low working voltage. The temperature sensing mechanism of the CNT sensor is explained in terms of the emission of CNT and the discharge properties of air.

2. Materials and Methods

Figure 1 shows the schematic illustration of the presented CNT-based temperature sensor. The sensor is comprised of three electrode plates; i.e., a CNT-based cathode, an extracting electrode, and a collecting electrode. The two ventilating holes in the cathode make the gas diffuse more easily [11]. A hole in the extracting electrode is used to extract discharge particles. A rectangular ditch in the collecting electrode could reduce reflection-induced loss of positive ions and collect more. In operation, the extracting voltage U_e is set higher than the collecting voltage U_c, where the potential of the cathode is 0 V. In this configuration, two electric fields E_1 and E_2 are generated with reversed field direction. The currents I_c and I_e were recorded by two high-precision digital multimeters (NI PXI-4071, National Instruments Corporation, Austin, TX, USA). One minute after the voltages are applied to the electrodes and the discharge of air is stable, ten current values of I_c and ten current values of I_e are recorded and averaged as currents I_c and I_e, respectively.

The presented CNT temperature sensor was fabricated according to the following steps. Three Si substrates were firstly patterned by photolithograph to form the pattern of the cavity with different sizes. The patterned substrates were then etched by an inductively coupled plasma (ICP) etcher. The etched structure included the cathode with two circular holes of 4 mm in diameter, the extracting electrode with a circular hole of 6 mm in diameter, and the collecting electrode with a rectangular ditch structure with the size of 8 mm × 6 mm × 200 µm (length × width × depth) (Figure 1a–c). A metallization layer of Ti/Ni/Au was then sputtered on both sides of the extracting electrode and the inner walls of the cathode and collecting electrode. Vertically aligned multi-walled carbon nanotubes (MWCNTs) were subsequently grown by thermal chemical vapor deposition (TCVD) on one side of the cathode at 700 °C [14], with around 20 nm in diameter, 5 µm in length, and separated with a distance of 200 nm in between (Figure 1d). The three electrodes were assembled with 50 µm-thick polyester films.

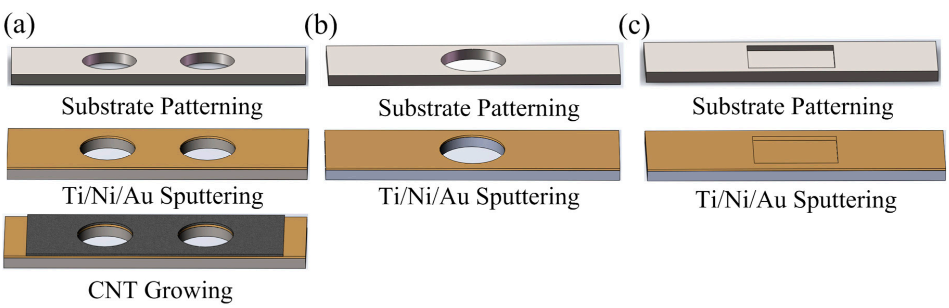

Figure 1. *Cont.*

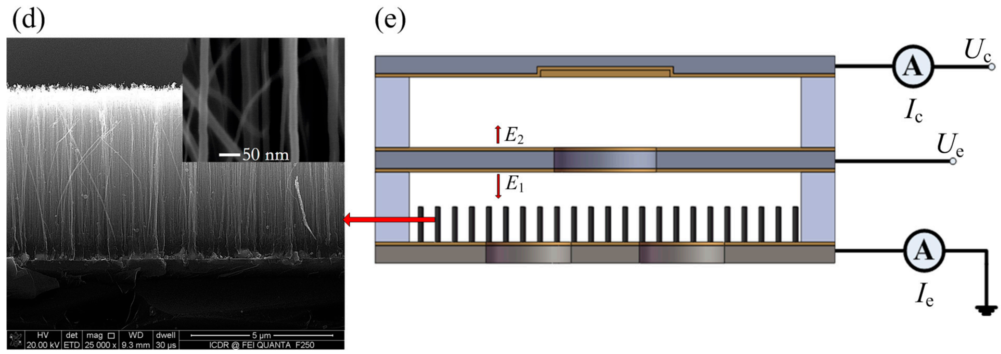

Figure 1. Scheme of the triple-electrode carbon nanotube (CNT)-based sensor. (**a**) the cathode after substrate patterning, Ti/Ni/Au sputtering, and CNT growing; (**b**) the extracting electrode and (**c**) the collecting electrode after substrate patterning and Ti/Ni/Au sputtering; (**d**) Scanning electron microscope image of the CNT film; (**e**) The test set-up.

3. Results

The effect of temperature on the discharge current of air was studied as depicted in Figure 1e. The fabricated sensor was placed inside a test chamber filled with ambient air heated by a resistive wire. The temperature inside the chamber was closed-loop controlled by tuning the voltage of the resistive heating wire and measuring the temperature using a k-type thermocouple (chromel–nisiloy). The steady state of the temperature was realized within the time of 1 min, in a range of 20 °C to 100 °C. After the temperature reached steady state, U_c of 1 V and U_e with values between 24 and 100 V were applied, and the discharge current I_c and I_e were measured respectively for the detection temperature and the study of emission properties of the CNTs cathode. When temperature T rose from 20 °C to 100 °C, currents I_c and I_e exhibited an exponential increase with T (Figure 2a,b). When extracting voltage U_e increased from 24 V to 100 V, currents I_c and I_e exhibited an increase with U_e. Sensitivity curves to temperature show very similar shape, as shown in Figure 2. This indicates that the sensor is sensitive to temperature and is thus capable of detecting temperature change. Values of I_e were almost twice of those of I_c. The temperature coefficients of Figure 2a were calculated according to equation $S = \Delta I/(\Delta T \cdot I_{FS})$, where ΔT is the variation of temperature, ΔI is the variation of I_c, and I_{FS} is the full scale range of I_c. The highest coefficient S_{max} was obtained as 0.04 K^{-1} at 100 °C and 24 V U_e (Table 1), higher than the values of other reported CNT-based temperature sensors [1–5].

Table 1. Performance comparison of the temperature sensors.

No.	Test Range (°C)	Highest Temperature Coefficient (K^{-1})	Reference
This paper	20–100	4.0×10^{-2}	-
Article 1	50–500	2.2×10^{-3}	[1]
Article 2	−269–147	-7.0×10^{-4}	[2]
Article 3	20–70	-1.3×10^{-2}	[3]
Article 4	20–75	-1.7×10^{-2}	[4]
Article 5	20–60	-5.0×10^{-3}	[5]

The relationship between the logarithm $\ln j_e$ (j_e is the cathode current density and is obtained by $j_e = I_e/S_{area}$) and the reciprocal $-1/T$ was studied (Figure 2c). S_{area} is the total cross-sectional area of all nanotubes on the film, and was calculated according to Figure 1d (Figure S3 in reference [15]); $S_{area} = 3.04 \times 10^{-6}$ m^2. Eight least squares straight lines were fitted to the curves of $\ln j_e - 1/T$ at different U_e, and the coefficients $R\text{-}Sq$ were calculated (Figure 2c)

$$R\text{-}Sq = 1 - (\Sigma(y_i - f_i)^2)/(\Sigma(y_i - y_{av})^2) \quad (1)$$

where y_i denotes $\ln j_e$, f_i denotes the fitting value to $\ln j_e$, y_{av} denotes the mean value of all $\ln j_e$, and subscript i denotes the sequence number. The coefficients R-Sq show that the straight lines are the best fit line to the curves at various U_e, indicating a thermal emission behavior of the sensor. The relationship between current density j_e and the average electric field E_0 was also obtained (Figure 2d), $E_0 = U_e/d$, where d denotes electrode separation between cathode and extracting electrode. j_e increased with E_0, showing a field-assisted thermal emission behavior [16].

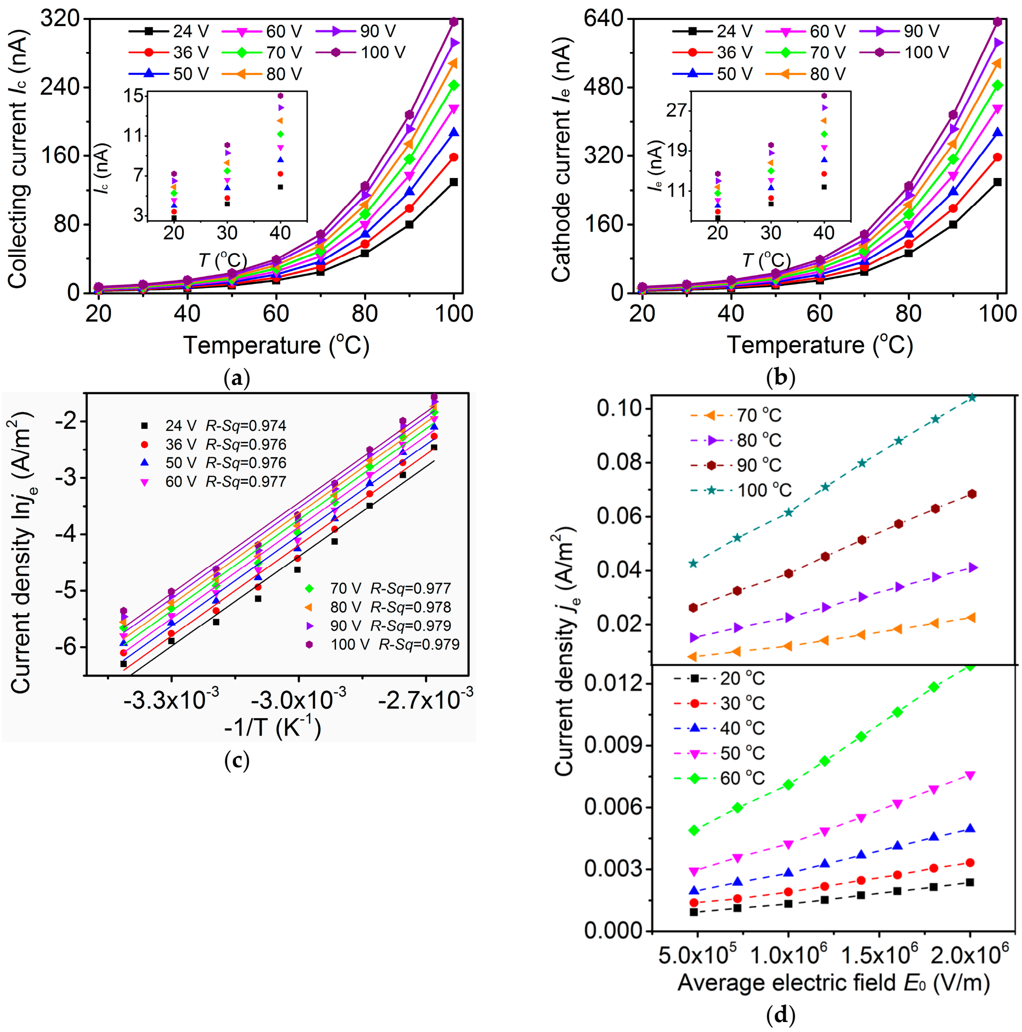

Figure 2. Effect of temperature on current at different U_e. (**a**) Collecting current–temperature characteristic and (**b**) Cathode current–temperature characteristic at 24–100 V U_e; (**c**) $\ln j_e$ increased linearly with $-1/T$ at 24–100 V U_e, suggesting the thermal emission behavior and a considerable effect of temperature on current density; (**d**) j_e increased with E_0, suggesting the field emission behavior.

4. Discussion

This section analyzes the experimental results to understand the temperature sensing mechanism of the present CNT temperature sensor. When U_e is applied, electrons are emitted from the nanotube tips and collide with the gas molecules, generating positive ions [17]. A fraction of the generated positive ions are extracted from the cathode region through the extracting hole towards the collecting electrode and form the collecting current I_c. Consequently, I_c is a part of the discharge current I [18], given by:

$$I = eN_0e^{\alpha d} \quad (2)$$

where e is the electron charge, N_0 is the number of electrons leaving the cathode in one second, and α is the first ionization coefficient. Emission electrons and secondary emission electrons of the CNT cathode contribute to N_0. In the non-self-discharge state, N_0 is mainly determined by the emission electrons [18]. It is known that only those electrons with energies greater than the sum of Fermi energy E_F and work function Φ can be emitted by the carbon nanotubes. When U_e is applied, the work function of electrons emitted by the CNT is reduced from Φ to Φ_{eff}. Φ_{eff} is the effective work function, and it decreased with increasing E_1 at a given temperature (Figure 3a). More electrons with energies greater than $E_F + \Phi_{eff}$ could be emitted by CNTs. It is well known that when temperature rises to T_2 and T_3 from T_1 (100 °C $\geq$ T$_3$ > T_2 > T_1), respectively, the probability of an electron gaining more energy increases (Figure 3b) [16]. As a result, more electrons leave the cathode at higher temperature and higher U_e, and form larger emission currentI_0 (I_0= eN_0) [19].The emission current density $J_{Schottky}$ could be expressed as follows [16]:

$$J_{Schottky} = B_0T^2 exp(-\Phi_{eff}/kT) \quad (3)$$

where B_0 is the Richardson constant and k is the Boltzmann constant. Since $J_{Schottky}$ is the main source of j_e, it is approximated in this work that $J_{Schottky} \approx j_e$, and exponential increase I_e with temperature could be obtained. The higher the temperature and U_e are, the larger are the cathode currents. The experimental results in Figure 2 are in good agreement with the above analysis.

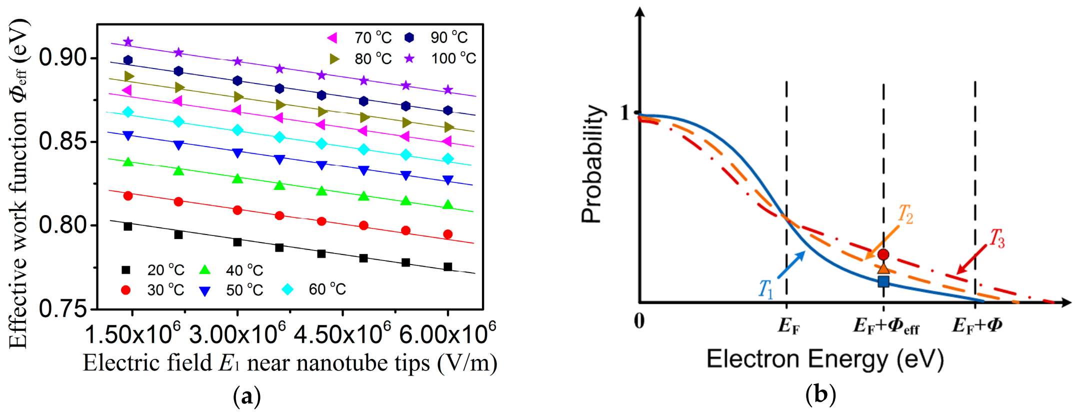

Figure 3. (**a**) The effects of the E_1 on Φ_{eff}; (**b**) The effect of temperature on the probability of an electron gaining energy.

Additionally, the first ionization coefficient α was also affected by temperature [17],

$$\alpha = exp(-U_i/(E\lambda))/\lambda \quad (4)$$

where λ is the mean free path of an electron, U_i is the first ionization potential of a gas molecule, and E is electric field.

$$\lambda = kT/(\pi r^2 P) \quad (5)$$

where k is the Boltzmann constant, r is the radius of gas molecules, P is gas pressure. α denotes the impact ionization ability of an electron with a gas molecule, which depends on E, λ, and U_i. Here, E does not change when electrode separation and applied voltage are given, and the first ionization potential U_i is a constant for a certain gas. As a result, α changes with λ. Since pressure P increases with temperature T at a fixed volume of the test chamber, λ does not change with temperature according to Equation (5). Therefore, rising temperature could not affect α in the experiment of this work. If the temperature sensor operates in an open environment, λ increases with temperature T at constant pressure P, and then the effect of temperature on α and discharge current should be considered.

5. Conclusions

In summary, a triple-electrode CNT-based ionization sensor was fabricatedby using micro fabrication technology. A vertically aligned multi-walled nanotube array was grown by thermal chemical vapor deposition on one side of the cathode. The relationship of currents I_c and I_e versus temperature was investigated in a wider test range of 20–100 °C and at 24–100 V U_e. The sensor in this work had a sensitivity of 0.04 K^{-1} at 24 V U_e, which is the highest sensitivity compared to the existing CNT-based resistive temperature sensors. The discharge current I_e and I_c increased with temperature, due to the increased number of electron emission at a given volume of gas mixture.

Supplementary Materials: The Supplementary Materials are available online at http://www.mdpi.com/1424-8220/17/3/473/s1.

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Author Contributions: Z.P. performed temperature effect experiment and wrote the paper. Y.Z. designed the project, supervised the experiments and modified the manuscript. Z.C., J.T., Q.C., J.P.Z. and J.X.Z. analyzed the data. Y.L. modified the manuscript and improved the English in the text. X.L. grew nanotube films.

Conflicts of Interest: The authors declare no conflict of interest.

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