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A high-integration sensor array sensitive to oxynitride mixture

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ABSTRACT

Measuring the concentration of oxynitride NO_x (including NO and NO_2) can provide a scientific basis for determining its potential harm to the human body. The existing metal oxide semiconductor sensor arrays are greatly limited by high operating temperature and low integration. In this article, we report on a high-integration carbon nanotubes sensor array with two different electrode separations sensitive to oxynitride mixture at low temperature. The triple-electrode sensor array is comprised of a large carbon nanotube array cathode, two extracting electrodes and two collecting electrodes and worked at non-self-sustaining discharge state, which was determined by the study on current-voltage characteristic of a double-electrode structure sensor. Through studying the relationship between gas concentration and discharge current at 1 atm, we obtained the distinct sensitivities of the binary mixture in the concentration ranges of 0–1166 ppm NO and 0–712 ppm NO_2 using the sensor array at low operating voltages and 60 °C. Collecting currents of the two sensors in the array decreased with increasing NO and NO_2 concentration in the gas mixture. The repeatable characteristics and dynamical response tests of the sensors were also conducted. The proposed sensor array has potential for the direct detection of a NO-NO_2 mixture without separating the mixed gases.

1. Introduction

As a major source of air pollution, NO_x (NO and NO_2) would not only cause great harms on the environment, but also generate harmful secondary particles like $PM_{2.5}$ and PM_{10} through physical and chemical reactions. Therefore, measuring concentration of NO-NO_2 mixture is of great significance.

The chromatography is a kind of traditional accurate monitor for gas mixture detection, but has the drawbacks of being very bulky and costly [1,2]. The metal oxide semiconductor sensor array has been reported for detecting gas mixture [3–5], but have been limited by several disadvantages like operating at high temperature (>300 °C) [6], and easy saturation [7,8]. For the past several years, carbon nanotubes (CNTs) have been considered as promising candidates for sensing materials to NO and NO_2 [9–11]. A chemical sensor based on individual single-walled carbon nanotubes was designed and its resistance decreased when it was exposed to 200 ppm NO_2 at room temperature [9]. Ueda et al. [10] fabricated a carbon nanotube based thin film NO sensor and the resistance of the sensor decreased when the NO concentration increased from 50 ppm (1 ppm = 1 μL/L) to 100 ppm at various given temperature values in a range of 25–250 °C. A multi-walled CNTs (MWCNTs) based gas sensor treated by laser irradiation showed better response than the unirradiated to 0–10 ppm NO at 150 °C [11]. The above sensors based on adsorption have been limited by narrow measuring range and a long time to response and recover (0.5–30 min) [7–9]. Ionization sensors using carbon nanotubes overcome the limitations above and exhibite low operating voltage, wider measuring range, lower operating temperature and fast response [12–18]. In this paper, we chose two different electrode separations for fabricating a two triple-electrode sensors array with carbon nanotubes grown on one cathode by using Microelectro Mechanical Systems (MEMS) technology, and conducted tests at low temperature and low operating voltage for detecting the two components of NO and NO_2 in a mixture with N_2 and synthetic air without component separation. The repeatable characteristics, dynamical response and the relation between the sensing response and the environment temperature tests of the sensors were also conduct for application.

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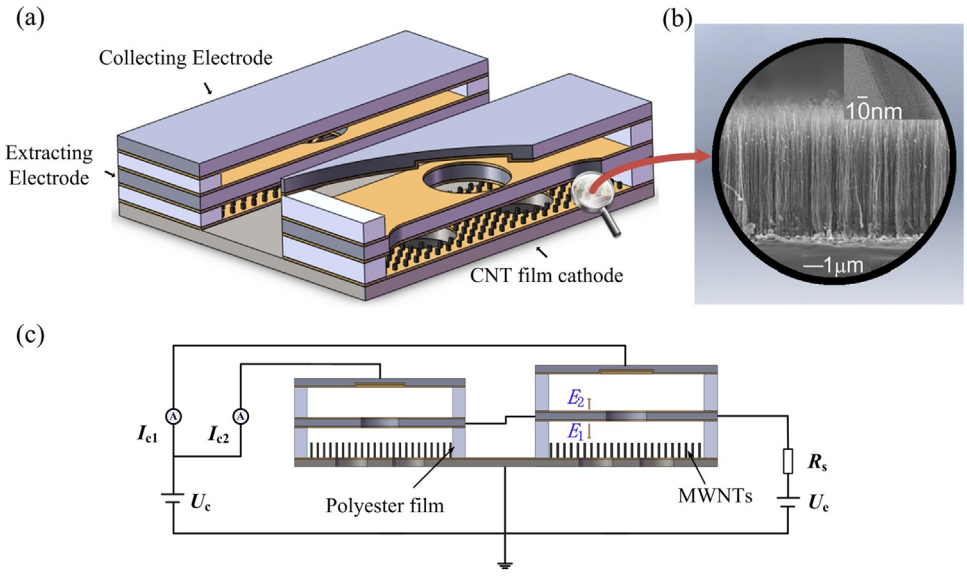

Fig. 1. The sensor array device. (a) Three-dimensional schematic of the device structure; (b) SEM micrograph of the carbon nanotubes; (c) Diagram of the actual test set-up.

2. Experimental details

Fig. 1 shows the details of our triple-electrode sensor array, which is comprised of two sensors with a large carbon nanotube array cathode (500 μm thick, 27 mm in length, 24 mm in width), two extracting electrodes and two collecting electrodes (500 μm thick, 27 mm in length, 8 mm in width). 50 nm thick Ti film, 400 nm thick Ni film and 125 nm thick Au film were sputtered on the both sides of the two extracting electrodes and the inner side of the cathode and two collecting electrodes. Then the five electrodes were rapidly annealed in a low vacuum of ~3.0 Pa at 450 °C for 50 s to alloy the Ti/Ni/Au film. The multiwalled nanotube (MWNT) array was grown by thermal chemical vapor deposition (TCVD) [19,20] on the inner side of the cathode. The nanotubes in the film are ~40 nm in diameter, and ~5–6 μm in length (Fig. 1b). The carbon nanotubes between the two sensors were removed by adhesive transfer method [21]. The distances between the cathode and the extracting electrode, and between the extracting and the collecting electrodes are the same. One sensor with 100 μm separations in the sensor array detected NO in a 0–1166 ppm range, and the other sensor with 120 μm separations detected NO_2 in a 0–712 ppm range. Controlled d.c. voltages of U_e and U_c (NI PXI-4132) are applied between the cathode and the extracting electrodes, and between the cathode and the collecting electrodes (Fig. 1b), respectively. U_e is higher than U_c, which generates two electric fields E_1 and E_2 in reversed field direction. The collecting currents I_{c1} and I_{c2} are measured by two digital multimeters (NI PXI-4071), and the resistor R_s is used to limit extracting current.

First, the effect of gas concentration on collecting current was studied. The sensor array was placed in a sensing cell (Fig. 2). Before the measurements, temperature was increased to 60 °C within 1 min by a temperature control device, and then the air was pumped out of the chamber by vacuum pump to establish a low vacuum with a gas pressure of 5 kPa. There were three gas cylinders containing high purity gas with concentration accuracy of 2%. One of them supplied the 99.999% environment gas N_2 and the others supplied the 0.5% NO and the 0.5% NO_2. Three mass flow controllers (MFC1, MFC2 and MFC3, Line Tech M3030 V with 1% accuracy) were used to continuously regulate gas flux for preparing the mixed gas concentrations. The full scales of the three MFCs were 1000 mL/min, 50 mL/min, 100 mL/min, respectively. After well mixed in a gas mixing chamber, gas mixture flowed into a sealable stainless steel sensing cell with a pressure meter to monitor gas pressure. Sixteen samples were tested while NO_2 concentration increased from 0 to 712 ppm at various given NO concentrations in a range of 0–1166 ppm.

3. Results and discussion

The working state of the triple-electrode sensors in the array is distinct from that of traditional double-electrode breakdown gas sensors [16–18]. Fig. 3 shows the current–voltage characteristic of a double-electrode sensor with 120 μm electrode separation in nitrogen at 1 atm and 23.7 °C. Non-self-sustaining discharge happened first, and then self-sustaining discharge developed, and a discharge current of 1.44 mA generated at the operating voltage of 350 V between the two electrodes. The carbon nanotubes were damaged due to the high discharge current density up to 474 A/m^2 with the area of CNTs calculated as 3.04×10^{-6} m^2, which would lead to a short operating life [22]. Therefore, the sensors using CNTs should keep working at non-self-sustaining discharge state by applying voltage below the breakdown voltage (350 V), which can reduce power consumption and extend the life-span of the sensors.

To understand the effect of electric field distribution and electrode separation as well as gas concentration on gas discharge current, analysis follows: The electric field E_{tip} near carbon nanotube tip is higher than the average electric field E_1 because of the high aspect ratio and the small radius of the curvature. The rate E_{tip}/E_1 is called an electric field enhancement factor γ and estimated according to the morphology of carbon nanotubes[23],

$$\gamma = 3 + 2(1+\eta)/\{(2+\eta)[2\pi(2+\eta)\delta^2 + \eta]\} \quad (1)$$

$$\eta = \rho/h \quad (2)$$

$$\delta = \rho/D \quad (3)$$

where ρ is the radius of a carbon nanotube, h is the height of a carbon nanotube, and D is the distance between the nearest carbon nanotube. According to Fig. 1b, ρ=20 nm, h = 6 μm, D = 100 nm, and then γ=5, E_{tip} = 5E_1. The enhanced E_{tip} could increase the number of the electrons emitted from the cathode [24]. The electrons collide with gas molecules, and most electrons and positive ions are produced near the tips. Through collision and diffusion, significant amount of the positive ions overcome the weak field E_1 near the extracting electrode and move into the region between the extract-