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Ambient temperature carbon nanotube ammonia sensor on CMOS platform

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Abstract

We report here the development of a resistive single wall carbon nanotubes (SWCNTs) sensor, based on a CMOS substrate that responds at ambient temperature to ppm levels of ammonia. The power efficient CMOS micro-hotplate is a thin membrane structure and comprises metal heater with an interdigitated electrode. The SWCNTs film was prepared first by treatment with aqua regia solution, followed by washing with distilled water, and then treated with ascorbic acid at 95°C. The film was deposited by simply dipping the chip into the solution. The SWCNTs showed good response to ammonia in a humid nitrogen atmosphere.

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Keywords: Single Wall Carbon nanotube; ammonia sensor; room temperature sensor; SOI CMOS, MEMS sensor

1. Introduction

There has been increasing demand for low cost (< $2), low power (< 20 mW) gas sensors to detect toxic gases and volatile organic compounds (VOCs). Commercial solid-state gas sensors (e.g. Taguchi) presently available consume

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too much power (~250 mW) and are expensive (average cost ~$25). The high cost is associated with sensors developed on non-CMOS platform, hence manufacturing process is not fully automated (no batch fabrication) and also a separate interface board is required. The high power consumption is because the sensing layer is made with metal oxides, which operate at high temperatures (300°C-500°C). Thus the motivation of this research work is to develop sensors on a CMOS platform, which will reduce the cost through batch fabrication and accommodation of on-chip electronics. A number of reported works [1-4] of CMOS-MEMS gas sensors is still relatively small and there are very few products available in the market. The power consumption of our sensor is reduced because it employs carbon nanotubes (CNTs) as sensing layer; CNTs can sense gases at room temperature.

In this paper, we report the synthesis of a single wall carbon nanotube film and its integration on CMOS-MEMS based low power micro-hotplate. The sensor showed excellent response in presence of ammonia at room temperature (~112% at 200 ppm ammonia).

2. Experimental

2.1 Micro-hotplate design

The gas sensor device contains a MEMS (microelectromechanical system) micro-hotplate structure. The micro-hotplates were designed using commercial software Cadence and fabricated using 1.0 µm SOI (silicon on insulator) CMOS process from a commercial foundry. The micro-hotplate consists of a micro-heater and interdigitated electrodes (IDEs). The micro-heater and IDEs were made with tungsten. They are separated by silicon dioxide insulating layer. The passivation layers over the IDEs were etched at the same time of bond pad creation. The bulk silicon underneath the micro-heater region was removed by deep reactive ion etching (DRIE) technique to realize the membrane structure. This helps in reduction of power consumption of the sensor device. The heater diameter is 150 µm and the overall membrane size is 562 µm. The sensing layers were deposited on top of the electrode to measure the resistance of the materials. A photograph of the fabricated device is shown in **Fig. 1(a)**. The cross sectional view of the device is shown in **Fig. 1(b)**. The hotplate consumes only 2 mW power to raise temperature up to 50°C. The details of the micro-hotplate and its power consumption have been reported elsewhere [3].

2.2 Single wall carbon nanotube film deposition

Single wall carbon nanotubes (SWCNTs) powder was purchased from Reinstate, India. First 5 mg of SWCNTs powder was kept in aqua regia solution for four days. The carboxylic acid groups were attached on the sidewall of

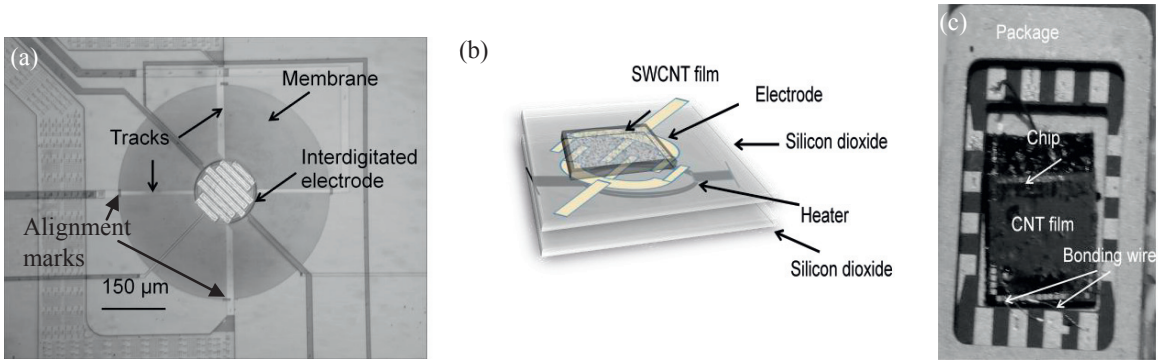


Fig. 1: (a) Optical microscope picture of the fabricated device. It contains CMOS micro-heater and interdigitated electrode. (b) Cross sectional view of the device. (c) CNT film was collected on the chip. The chip was bonded on a package

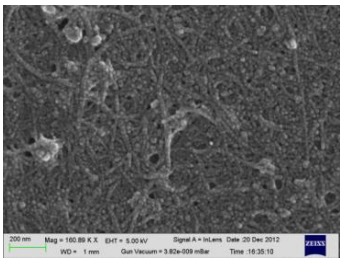
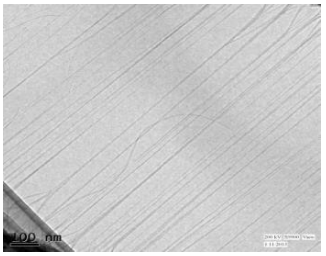
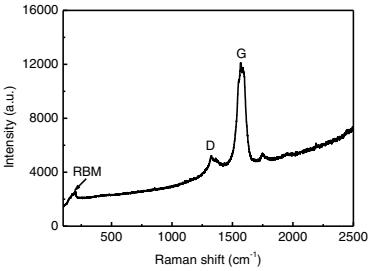


Fig.2. (a) Scanning electron microscope picture of carbon nanotubes.



(b) TEM image of carbon naotubes



(c) Raman spectra of the SWCNT film showing as expected the radial breadth mode (RBM), D and G lines.

the carbon nanotube due to the aqua regia treatment [5] that makes them water soluble. Then the CNTs were filtered and washed with deionised (DI) water several times until the solution becomes neutral (pH value 7.0). CNTs powder was dispersed in water using a sonicator and then 20 mg of ascorbic acid was added to the solution. The solution was kept at 95°C. After some time the film started floating on the solution. A small film was collected on the CMOS-MEMS devices and dried up in air. Then the devices were bonded on a 16 pin DIL packages which is shown in **Fig. 1(c)**.

3. Results and discussions

The CNTs were characterized using a field emission scanning electron microscopy (FESEM) (supra 40, Carl Zeiss Pvt. Ltd. Instrument), transmission electron microscopy (TEM) (H-9000 NAR, Hitachi) and Raman spectroscopy (Renishaw Raman Microscope). The FESEM image of the CNT film was shown in **Fig. 2 (a)**. It shows the CNTs are entangled with one another to form an electrically conducting film. A TEM picture of the nanotube was shown in **Fig. 2(b)**. Raman measurement of this film was shown in **Fig. 2(c)**. A clear distribution of the radial breadth mode was seen in the Raman spectra which indicate the presence of SWCNTs.

Sensor performance was measured in the presence of ammonia using an in-house built gas test chamber. The details of the sensor set up were reported in [6]. The sensing was performed at room temperature and also at 50°C. The results are shown in **Figs. 3(a)** and **(b)**. The concentration of ammonia was varied from 200 to 1400 ppm. The measurements were performed in humid nitrogen environment. The sensor was initially kept for 20 minutes in nitrogen environment to stabilize the baseline resistance. Then the ammonia was ON for 10 minutes and OFF for 15 minutes. The sensor response (R) in percentage was calculated using the following equation.

$$R\% = \frac{R_{NH_3} - R_{N_2}}{R_{N_2}} \times 100$$

where R_{NH3} is the resistance of sensing layer in presence of ammonia and R_{N2} is the resistance in nitrogen. The sensor response decreases with increasing operating temperature as shown in **Fig. 3(b)**. The response was found to be 112% at 200 ppm, *ca*. 0.6%/ppm at room temperature; whereas, in the case of 50°C the response is only 22% at 200 ppm, *ca.* 0.1%/ppm. However, the desorption of attached analytes from the CNT surface is much better at higher temperature. So, one can see that there is good base line recovery of sensor device at 50°C compared to at room temperature.

The resistance of the film increases as ammonia inserted in the chamber. Carbon nanotubes are known to be a *p*-type material and ammonia has electron donating capability. So with increase in ammonia concentration, the hole concentration in CNTs decreases, this in turn results in increasing film resistance. The response we observed is higher compared to the recently reported results [7, 8]. We believe this is due to the attachment of the carboxylic acid groups on the sidewalls of CNTs which act as active sites for ammonia interaction.

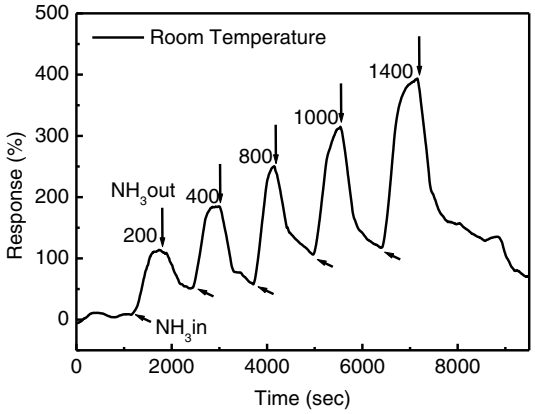
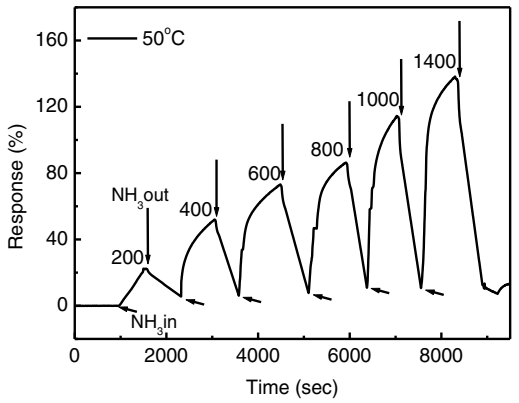


Fig. 3(a) Response (%) of the CNT film to ammonia gas at room temperature. Ammonia concentrations ranged from 200 – 1400 ppm.



(b) Response (%) of the CNT film to ammonia gas at 50°C.

4. Conclusions

A single wall carbon nanotube based ammonia sensor has been developed on a fully processed CMOS substrate. The CNT film was synthesized, functionalized (with carboxylic acid groups) and collected directly on the SOI CMOS micro-hotplates. It was found that the CNTs showed a high sensitivity towards ammonia at room temperature, with the sensor consuming very low power. We believe work on such low-power low-cost sensors will be useful for the future development of ammonia sensors.

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