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Scalable fabrication of individual SWNT chem-FETs for gas sensing

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Abstract

We present a scalable, Deep-UV (220 nm) photolithography based process for fabricating low-power gas sensors integrating an individual single-walled carbon nanotube (SWNT) as a sensing element. SWNTs grow from defined catalyst (ferritin) islands, and their density is controlled by controlling the catalyst particle density. By designing the electrode dimensions based on the length distribution of SWNTs, a single-SWNT bridging yield of 30% has been achieved. Furthermore, we show that exposure to NO_2 at room temperature results in a positive shift of the threshold voltage. A threshold shift of approximately 2V for 500 ppb of NO_2 is observed. The presented process also enables the possibility of fabricating carbon nanotube sensor arrays, as a large number of single-tube devices can be fabricated in each process run.

Keywords: Carbon nanotubes; gas sensors; scalable;sensor array

1. Introduction

It is well-established [1] that carbon nanotubes and in particular, individual single-walled carbon nanotubes exhibit promising gas sensing properties such as ultra-low power, room temperature operation and low limits of detection. Building arrays of such individual CNFETs can enable the collection of statistical data as well as lead to low-power sensor arrays. If this can be achieved with a scalable process,

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improvements in selectivity (through functionalized arrays) and noise performance (due to ensemble averaging) of CNFET-based gas sensors can be expected.

In the following study, we present a fabrication process which utilizes standard photolithography and SWNT growth by chemical vapor deposition from ferritin-based iron nanoparticles, which enables the fabrication of moderate-yield carbon nanotube gas sensor arrays.

2. Fabrication

A p-doped silicon substrate serves as the back gate, on which 70 nm of dry thermal oxide is grown to serve as the gate oxide. Initially, markers are patterned by reactive ion etching. After patterning holes with Deep-UV (DUV) contact lithography, the catalyst precursor (ferritin) is adsorbed onto the substrate, followed by lift-off which results in localized catalyst particles for SWNT growth at 850 °C in CH_4/H_2. Ferritin is the preferred catalyst source because it provides control over the SWNT density on the surface [2], as well as a narrow SWNT diameter distribution [3]. Metal electrodes are patterned through a DUV lift-off process. The entire device is passivated with 40 nm of Al_2O_3 deposited via atomic layer deposition at 300 °C, which results in stable electrical characteristics [4]. Finally, the passivation layer is removed in the middle of the SWNT channel through a buffered HF (6%) etch, exposing a 500 nm segment out of 2 µm of the SWNT channel to gas. This results in contact-passivated, open-channel CNFET gas sensors.

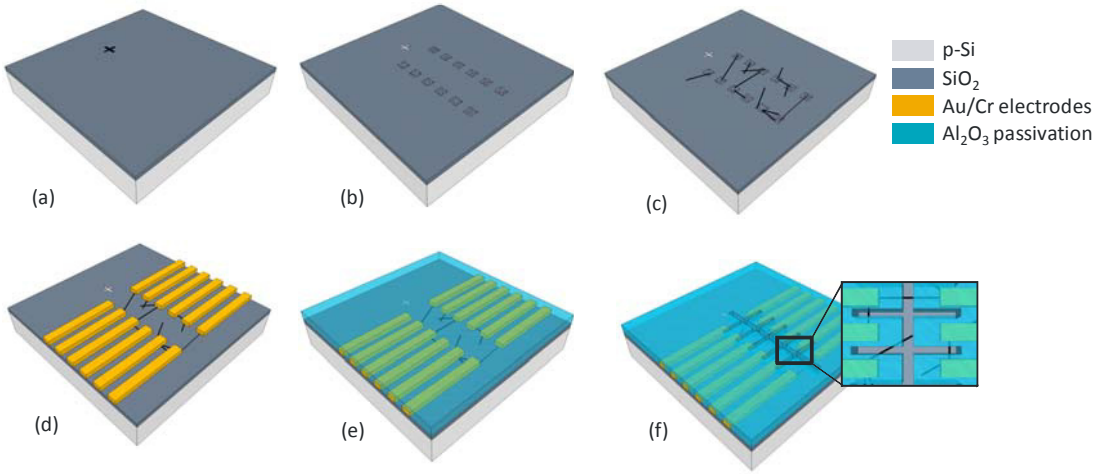


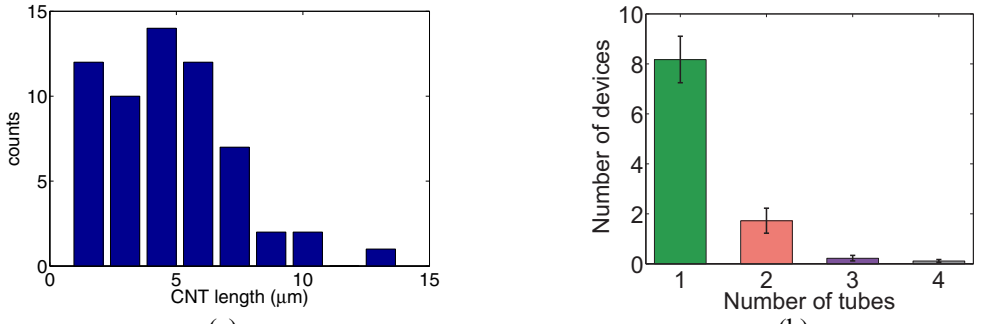
Fig. 1 (a) Scalable fabrication process flow for fabricating SWNT arrays. (a) marker etch (b) definition of catalyst islands followed by ferritin adsorption at defined density (c) CNT growth at 850°C (d) Cr/Au metal electrode patterning by lift-off (e) ALD passivation (f) gas access window opening.

3. Electrode design

The electrode gap was designed based on the measured CNT length distribution. A typical length distribution measured with atomic force microscopy (AFM) is shown in figure 2a. The distribution is fitted in MATLAB with a Weibull distribution. These parameters were subsequently used in Monte Carlo simulations to generate CNT lengths, while sampling the number of CNTs per island from a Poisson distribution. The connectivity to the electrode arrays was analyzed to obtain the number of CNTs

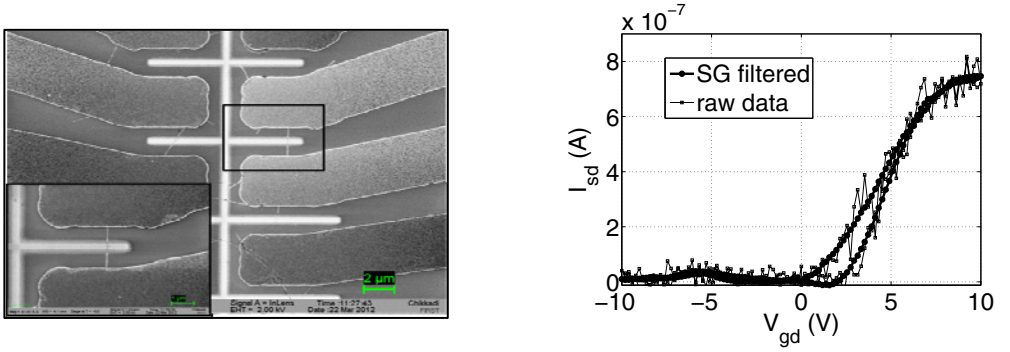
bridging across electrodes. Connections forming loops across electrodes and tube-tube intersections were explicitly excluded. The bridging yields were estimated for different electrode gaps.

For a catalyst island of 2 µm x 4 µm with an inter-electrode gap of 2 µm and a density of about 3 CNTs/island, about 7-9 bridging nanotubes were obtained per set of 20 electrodes, resulting in a yield of about 30 % (figure 2b).



(a) (b)

Fig. 2 (a) Length distribution of grown CNTs measured with AFM. This distribution was fitted with a Weibull distribution and the parameters of the fit were utilized in Monte Carlo simulations to obtain bridging yields. (b) Results of the bridging simulations- the standard deviation is plotted as the error bar around the mean. The number of single-bridging CNTs is approximately 8 (±1), while a small number (1.5-2.5) of double and triple-bridging events are observed in simulation.



(a) (b)

Fig. 3 (a) Scanning electron micrograph of the fabricated array of carbon nanotube-based transistors. The metal electrodes, as well as the opening across the carbon nanotube channel are clearly visible in the inset. (b) Electrical transfer characteristics for a forward and reverse gate sweep of one such carbon nanotube sensor with an open channel in dry air. Effect of the Savitzky-Golay (SG) filter in eliminating noise while maintaining features such as the threshold voltage is observed.

4. Results and discussion

The results of the fabrication process flow are shown in figure 3a. The carbon nanotubes bridging across patterned electrodes with an open channel can be clearly seen. Once the devices were fabricated, they were electrically characterized with the pulsed gate sweep technique outlined in [5]. However, the hysteresis is not completely suppressed, indicating residual charge trapping in the device at 1ms pulse widths which may be attributed to fast traps surrounding the CNT arising due to processing residues. Lower pulse widths may further help minimize hysteresis. To simplify data interpretation, the electrical measurements were filtered with a Savitzky-Golay low-pass filter (figure 3b) which preserves the general features of the curve, while eliminating electrical noise.

Transfer characteristics for an n-type device seen in figure 3b were obtained by sweeping the gate voltage and recording the drain current at 1-minute intervals. The results of gas measurements are shown in figure 4. Exposing the SWNT transistors to a nitrogen flush to eliminate oxygen results in a negative shift of the threshold voltage. A positive shift of the threshold voltage is seen upon exposure to 500 ppb NO_2. No shift is discernible at 50 ppb, indicating that the detection limit is above this value. It is expected that heating or UV-illumination can recover the sensor baseline [1].

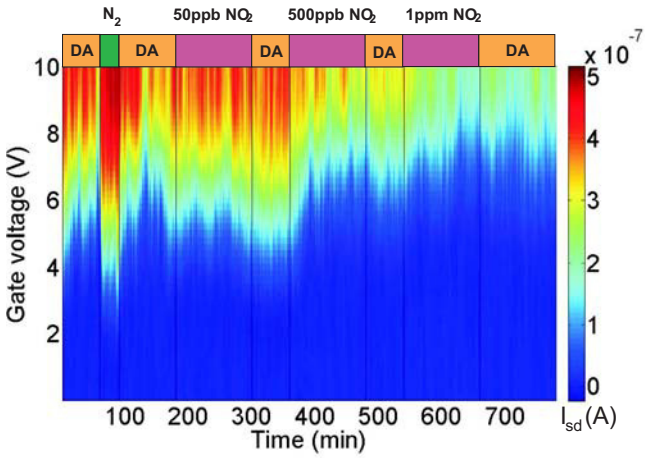


Fig. 4 Gas measurements with an n-type transistor. Positive gate voltages, (both forward and reverse sweep) are shown. The SG-filtered drain current I_{sd} (color) measured against gate voltage and time indicates an n-type device with an initial threshold voltage around 5V. The scheme of the gas measurement is shown above the plot. DA: Dry air. Upon introduction of nitrogen, a negative shift of the threshold voltage is seen. This is expected due to removal of oxygen (a p-dopant) from the chamber. Upon introducing NO_2, a positive shift of the threshold voltage is observed. No clear shift is observed for 50 ppb concentration, while a shift of approximately 2V is observed for 500 ppb and a further shift of approximately 1V for 1 ppm.

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