Nanoelectronic CO_2 Breath Sensors

A. Star*, V. Joshi, D. Thomas, J. Niemann, J.-C. P. Gabriel and C. Valcke

* Nanomix Inc., Emeryville, CA, astar@nano.com

ABSTRACT

Application of chemical recognition layers to carbon nanotube field effect transistors (NTFET) can induce specificity to analytes of prime interest. In particular, employing pH sensitive polymer layers provides a facile route for the accurate detection of CO_2 gas. Coupling the scalable processes for NTFET device fabrication and site-specific polymer deposition can provide an accessible method for producing thousands and even millions of tiny, robust gas sensors for airway monitoring.

Keywords: carbon dioxide, carbon nanotubes, field-effect transistors, polymers, sensors

1 INTRODUCTION

The measurement of carbon dioxide levels in respiration is a standard of care or guideline according to the American Heart Association, the American Association of Respiratory Care, and the American Society of Anesthesiologists, and is a primary tool in the monitoring and management of respiratory function [1]. Nanomix develops nanotechnology based capnography sensors for the measurement of carbon dioxide in human respiration.

Field-effect transistors fabricated using carbon nanotubes (NTFETs) [2] have been recently explored as chemical [3,4] and biological [5] sensors. The response of the device characteristics to chemical analytes occurs through charge transfer between the NTFET and the analytes, as evidenced by experiments involving electron donating (NH_3) and electron withdrawing (NO_2) molecules [3]. Recent studies also demonstrate the effect of electron negativity of aromatic compounds on NTFET electronic characteristics [4]. Whereas the bare NTFET devices are sensitive to the presence of strong charge donors and acceptors, they are not sensitive to weak Lewis acids or bases such as H_2, CO_2, and CH_4. Specific sensitivity can be achieved by employing recognition layers that induce chemical reactions that modify the NTFET device characteristics.

2 RESULTS

For the CO_2 selective recognition layer, we have used a mixture of poly(ethylene imine) (PEI) and starch polymers. The change in the device characteristic upon CO_2 exposure can be used for sensor design. The chemical reactions lower the total pH of the polymer layer and alter the charge transfer to the semiconducting nanotube channel, resulting in the change of NTFET electronic characteristics (Figure 1). The response to CO_2 gas is fast and reproducible at low concentrations, and has a wide dynamic range, from 500 ppm to 10% CO_2 in air [6].

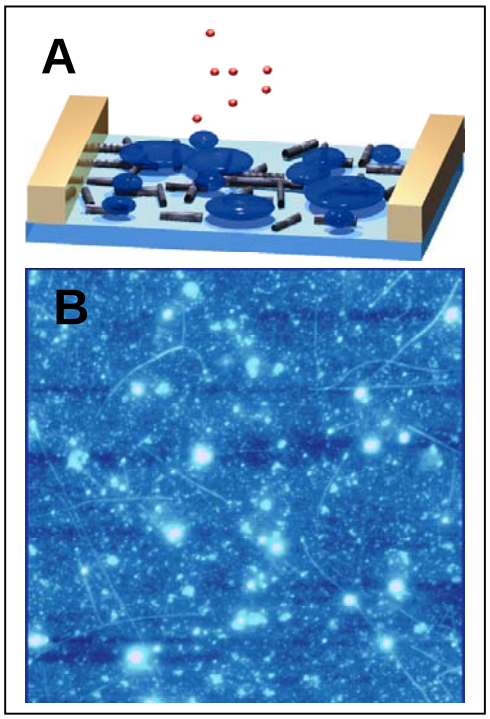

Figure 1: (A) Conceptual drawing of a carbon nanotube network device coated with polymer layer for CO_2 detection. (B) Atomic Force Microscopy (AFM) image of network of carbon nanotubes functionalized with a polymer layer for CO_2 sensing [6].

2.1 CO_2 Gas Testing Fixtures

We test sensors by using the Functional Test Board (FTB). The FTB is the culmination of an engineering research effort to characterize and test large numbers of functionalized NTFET devices, thereby evaluating their gas sensor properties. The FTB design included multiplexers to test up to eight packaged die, thus allowing measurement of a total of ~120 sensors per load (Figure 2A). All board configuration is under PC software control. Gas manifolds are attached directly to the socket board and the temperature, relative humidity, and air content are measured. The gas delivery is PC-controlled and implemented by mass-flow controllers. Labview software is used to program the test, and the test results are uploaded to Nanomix's database. The tests were designed to evaluate the CO_2 sensor's resolution and reproducibility in a specified wide dynamic range (Figure 2B and C).

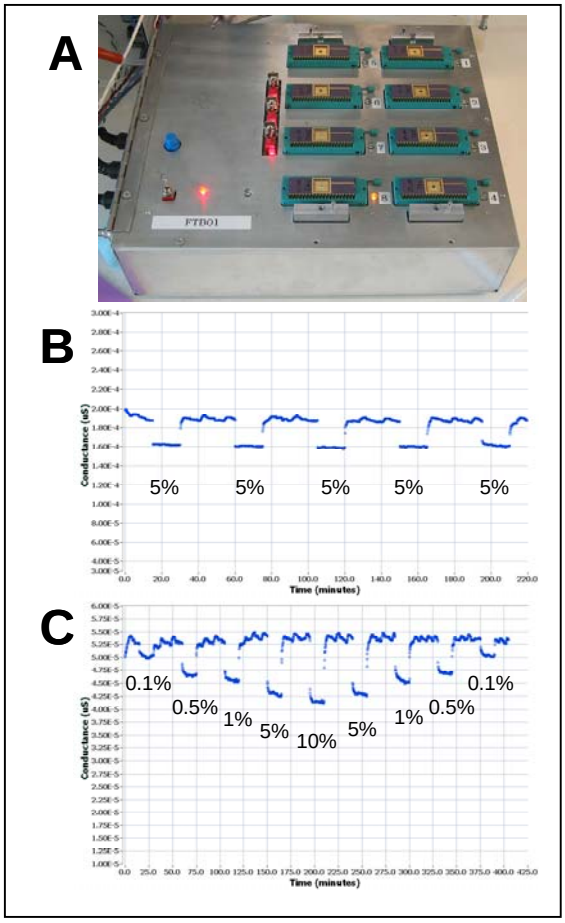

Figure 2: (A) Photograph of the Functional Test Board (FTB) loaded with eight packaged die containing functionalized NTFET devices. (Gas manifolds are removed to expose the packages). (B) FTB data presenting sensor response to five exposures of 5% CO_2 gas in air at fixed temperature and relative humidity. (C) Sensor response to variable CO_2 gas concentrations at 80% RH.

2.2 Data Analysis

Multiple CO_2 tests were conducted with relative humidity levels alternating between 40% and 80% from test to test. To fit the response of a sensor and separate the effect of CO_2 from that of humidity, we used the following model:

$$G = k_0 + k_1P + k_2RH + k_3PRH + \varepsilon \quad (1)$$

where G is conductance of the nanotube device, P is partial pressure of CO_2, RH is relative humidity, and ε is error of the fit.

The model then was simplified by backward elimination and the remaining predictors orthogonalized by Gram-Schmidt method. A sensor was considered to be responding to CO_2 if the absolute value of partial correlation between G and P was above 0.5. We also checked that the probability for observed correlation was below 0.05. Yields were calculated as the proportion of sensors that respond to CO_2 according to the above criteria to the total number of sensors in a given category.

2.3 Sensor Optimization

Nanomix explored and refined the process conditions needed to fabricate nanotube devices on 4" silicon wafers. During the effort, different electrode geometries and carbon nanotube densities were evaluated in order to optimize the sensor platform in terms of CO_2 response. Modifications in the sensor platform resulted in changes in the transducer electronic characteristics and its subsequent response to CO_2 gas.

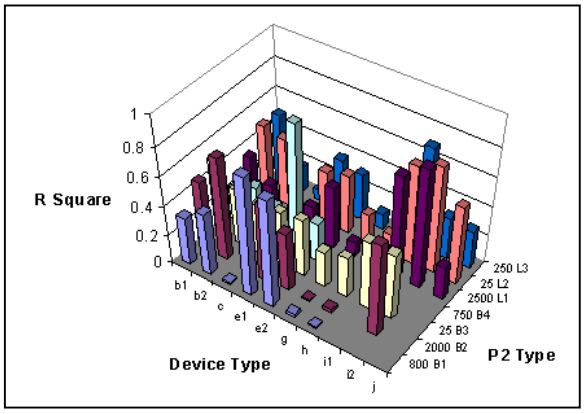

Figure 3: 3-D plot of correlation factor (R Square) as a function of polymer formulations (P2 Type) and nanotube device structures.

Different formulations of the polymeric recognition layer have also been explored. Depending on the chemical composition of the polymer layer, different sensor sensitivity and long-term stability was observed. The methods of polymer deposition were also found to have an effect on the sensor performance. Among different deposition methods, spin-coating of the polymer can produce an uniform recognition layer in a scaleable process. The polymer layer thickness as measured by the profilometer can be tuned by spin-coating parameters, such as spin speed and concentration of the polymer solution.

2.4 Sensor Integration

In order to gain a more realistic measure of our capnography sensors, a laboratory prototype was developed. The prototyping unit was constructed on a printed circuit board with measurement electronics and a serial (RS-232) port for computer interfacing. A program running in LabVIEW communicated with the prototype from a laptop PC. The sensor chip was packaged into a 16-pin CERDIP (ceramic dual inline package) and enclosed with a PTFE filter to limit possible exposure to bodily fluids such as saliva. A breathing tube, mounted onto the filter, allowed for an unobstructed airway in which one could breathe.

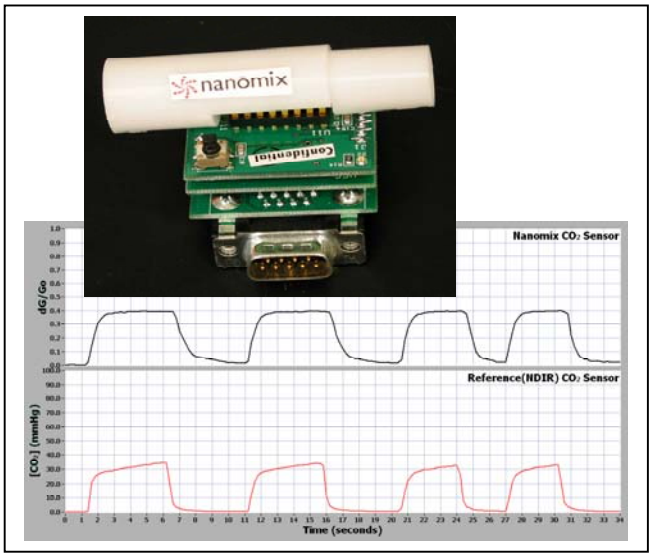

Figure 4: Operation of Nanomix prototype (shown in picture) in comparison with state-of-the-art NDIR CO_2 monitor (not shown) during four normal breaths.

To better judge Nanomix sensor's performance, a sidestream NDIR (non-dispersive infrared) CO_2 monitor (CO_2 Waveform Analyzer, CardioPulmonary Technologies, Inc.) was placed in series with the prototype and connected to the PC (RS-232). The signals from both our prototype and the sidestream monitor were displayed in LabVIEW (Figure 3). This allowed for a good comparison of our CO_2 sensor to one that is commercially available. The Nanomix sensor not only gives an estimation of end tidal CO_2, but also presents useful waveform data.

3 DISCUSSION

Wafer level functionalization using CO_2 sensitive polymers is performed using variety of deposition techniques such as spin-coating, spraying, etc. Although these techniques allow uniform polymer layer formation on silicon wafers, patterning of the polymer on NTFET devices still remains challenging. For fabrication of capnography sensors, polymer functionalization should be deposited only NTFET devices, which occupy areas of several microns in size; the rest of silicon wafer containing metal electrode contacts and wire-bonding pads should remain uncovered. Ink-jet dispensing provides rapid and convenient methods for advanced deposition of polymer based coatings, allowing for the production of features that range in scale from micrometers to millimeters and with a good control of the thickness of the deposited film. The method enables the deposition of aqueous and organic solvent based polymer mixtures on to solid and flexible substrates and either at room or elevated temperature. For capnosensor-specific developments, it is essential to determine the deposition quality for individual process parameters, particularly for new polymeric materials, which are part of the sensing and encapsulation layers. This activity is done by determining the thickness of the deposited layers, which can range from a few microns down into the nm range. Measurements of layer thickness during the process are the prerequisite for successful layer development. At the same time, it is important to maintain a homogeneous layer thickness over the total area to guarantee proper manufacturing and operation. We foresee that instituting this level of control and quality will ensure highly performing devices that will meet the necessary requirements for medical monitoring.

4 MEDICAL APPLICATIONS

This Nanomix sensor, currently under development, will significantly extend the reach of CO_2 detection and broaden the application of general airway monitoring [7]. These nanoelectronic sensors represent a new generation of low-cost, low-power carbon dioxide gas sensors embedded in disposable adapters that fit directly into the patient airway (Figure 5). By applying scalable semiconductor fabrication techniques, Nanomix can produce these high quality sensors in large volumes. This monitoring device can be embedded into standard airway adapters, masks, resuscitation bags or multi-parameter systems. A display linked to the device continuously monitors CO_2 concentration and end tidal values or can report other respiratory information. The sensor has a wide dynamic range, 0-10% CO_2, and the needed accuracy, 0.5%, for true quantitative monitoring. Additionally, the response time of

the device is well under 1 second, sufficient to track the fastest breathing rates.

The construction of the sensor assembly will be flexible to address most airway monitoring environments. The device will be applied in hospital, prehospital, and out-of-hospital settings. The versatile technology allows Nanomix to provide highly valuable monitoring information to all health care providers whether they are doctors, nurses, respiratory technicians, or paramedics. The Nanomix CO_2 sensor will provide significant healthcare benefits by providing respiratory monitoring for endotracheal tube verification, intra/inter hospital transport, adequacy of CPR, sleep apnea screening, procedural sedation monitoring, metabolic testing, asthma monitoring, and many others. The initial Nanomix respiratory monitor has been optimized for the Emergency Medicine customer. This small, noninvasive, and disposable in-line detection device continuously monitors varying CO_2 levels and delivers accurate measurement of end tidal carbon dioxide concentrations. The device will have a bar graph to continuously track CO_2 concentration. The operating lifetime of the sensor, 6 hours, is more than enough to accommodate long transport times.

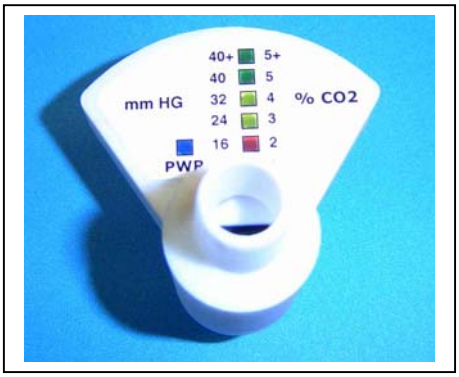

Figure 5: Photograph of a mock-up capnography device.

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