Integration of metal oxide nanobelts with microsystems for nerve agent detection

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We have assembled tin dioxide nanobelts with low-power microheaters for detecting dimethyl methylphosphonate (DMMP), a nerve agent simulant. The electrical conductance of a heated nanobelt increased for 5% upon exposure to 78 parts per billion DMMP in air. The nanobelt conductance recovered fully quickly after the DMMP was shut off, suggesting that the single-crystal nanobelt was not subject to poisoning often observed in polycrystalline metal oxide sensors. While the sensitivity can be improved via doping nanobelts with catalytic additives, directed assembly or growth of nanobelts on microsystems will potentially allow for the large-scale fabrication of nanosensor arrays. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1861133]

Metal oxide sensors are commonly used to monitor a variety of toxic and inflammable gases in an air pollution monitoring system, food industry, medical diagnosis equipment, and gas-leak alarms. The sensing mechanism is based on electrical conductance change upon surface reduction-oxidation (redox) reactions with gas species.[1] Because only the surface layer is affected by the reaction, the sensitivity of a metal oxide sensor increases for decreasing thickness, motivating the development of thin film metal oxide sensors. However, one common problem with polycrystalline thin film metal oxide sensors is grain boundary poisoning that limits the repeatability and long-term stability.[2,3]

Recently, single-crystal ribbon- or belt-like metal oxide nanostructures have been synthesized.[4] Because the nanobelts are as thin as 10 nm, almost the entire thickness is affected by redox reactions with gas species. In an earlier work,[5] a bunch of tin dioxide (SnO_2) nanobelts deposited on prepatterned metal electrodes were tested for gas sensing. When the nanobelts were heated using a thin film heater deposited on the backside of the wafer, the electrical conductivity decreased for about 20 times upon exposure to 0.5 parts per millions (ppm) nitrogen dioxide (NO_2) balanced with air.

Metal oxide sensors require a high operating temperature to enhance redox reactions so as to achieve the optimum sensitivity. This requirement has motivated us to integrate nanobelts with thermally isolated suspended microfabricated heaters that can reduce the power consumption so that battery-operated miniaturized sensor arrays can be obtained. More importantly, a major challenge for the development of sensor technologies based on nanobelts or other "bottom-up" synthesized nanostructures is the large-scale manufacturing of well-organized nanostructure sensor arrays. In this letter, we report the assembly of nanobelts with "top-down" fabricated microsystem devices and the use of the as-assembled sensor to detect dimethyl methylphosphonate (DMMP), a nerve agent simulant. DMMP of a concentration as low as

about 50 parts per billion (ppb) can be detected by the sensor, and we found that sensor poisoning was eliminated when a good electrical contact to the nanobelt was made. This experiment is a step towards the large-scale integration of nanomaterials with microsystems, and the integration can potentially allow for the fabrication of low-power, sensitive, and selective nanosensor arrays.

Figure 1 shows a microheater device that consists of two adjacent silicon nitride (SiN_x) membranes.[6] Each membrane is supported by long, low-thermal conductivity silicon nitride (SiN_x) beams and thermally isolated from the substrate. The temperature of the membrane can be increased and monitored with the use of a serpentine platinum (Pt) resistance thermometer (RT) line patterned on the membrane. With only 3.8 mW power consumption in the Pt RT, the membrane temperature can be raised to 500 °C.

Two parallel Pt contact electrodes are patterned on the two adjacent membranes. We have investigated two methods
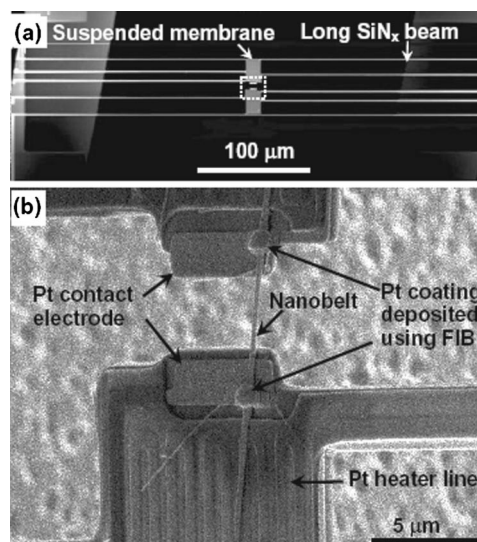

FIG. 1. (a) Scanning electron micrograph of the microheater device, (b) an enlarged image showing the region inside the white dashed rectangle in (a).

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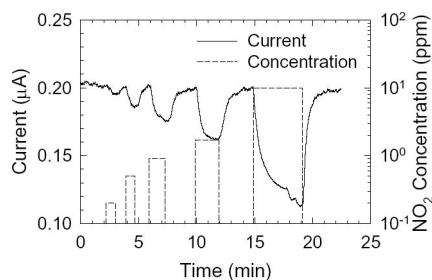
FIG. 2. Response of the as-assembled nanobelt-MEMS sensor to 0.2, 0.5, 0.9, 1.7, and 10 ppm NO_2 balanced with air when the nanobelt temperature was 200 °C. The voltage applied to the nanobelt was 2 V.

FIG. 3. Response of the as-assembled nanobelt sensor to 78 and 53 ppb DMMP balanced with air when the nanobelt temperature was 500 °C. The voltage applied to the nanobelt was 1.5 V.

to trap nanobelts on the pair of electrodes. In the first one, a solution containing the nanobelts was spun on a wafer that contained a large number of densely packed membrane structures. When nanobelts were uniformly deposited on the wafer from the solution, it was found that nanobelts were often adsorbed between the two closely spaced Pt electrodes while no nanobelts were left bridging the long SiN_x beams far apart from each other. To increase the assembly yield, we have investigated an electric field-directed assembly method. In this method, the two Pt electrodes in the microdevice were connected to an ac voltage source. As a solution containing the nanobelts was dispersed on the wafer surface, the frequency of the ac field was adjusted to generate an attractive force on the nanobelts that were polarized in the electric field. This phenomenon is called positive dielectrophoresis, where a polarizable particle in a nonuniform ac electric field is attracted to regions of high field strength.[7] The attractive or positive dielectrophoretic force can be used to align and trap a nanobelt onto the two Pt electrodes. We found that the suitable frequency and root-mean-square (rms) amplitude of the ac voltage were about 1 MHz and 5 V, respectively, for trapping the nanobelt. Similar methods have been reported for trapping nanotubes[8] and nanowires[9,10] with a yield approaching 100%. In our experiments, usually several nearly parallel nanobelts were trapped between two adjacent electrodes.

We have tested the device shown in Fig. 1 that had only one nanobelt trapped between the two Pt electrodes. We used a focused ion beam (FIB) method to deposit a thin Pt coating on the contact location between the nanobelt and each Pt electrode so as to improve the electrical contact. The sensor was mounted in a small flow-through chamber and tested with NO_2 and DMMP gases diluted in air.

Figure 2 shows the response of the nanobelt sensor to 0.2–10 ppm NO_2 gas balanced with air while the nanobelt was heated to 200 °C by the microheater. Current change in the nanobelt was clearly observed when the NO_2 concentration was as low as 200 ppb. The sensitivity can potentially be improved with the optimization of the heater temperature and with the doping of the nanobelt with catalytic additives to increase its electrical conductivity and enhance redox reactions.[3]

This single nanobelt provides a model system for us to investigate the sensor poisoning effect. We found that the current through the nanobelt recovered fully quickly after the NO_2 gas was shut off and the flow-through chamber was purged with room air. The recovery was much faster than that of the bunch of nanobelts tested in the earlier work. It took less than 3 min, which could be the time required for
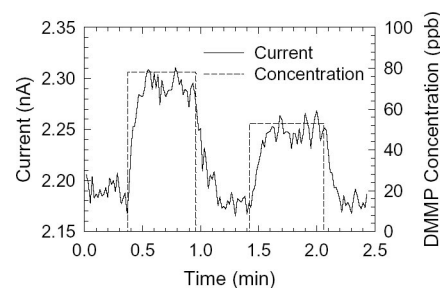
completely purging NO_2 out of the flow-through chamber, for the single nanobelt sensor to be refreshed. On the other hand, the bunch of nanobelts in the earlier work was not completely refreshed 40 min after the NO_2 gas was shut off.

The faster recovery observed in the nanobelt is due to the absence of grain boundaries or interfaces along the single nanobelt of a single-crystal structure. In fact, we found that the Pt coating deposited on the two nanobelt-electrode contact locations by the FIB method was critical for eliminating the sensor poisoning effect. Without this contact treatment, it was observed that even a sensor consisting of just a single nanobelt could be poisoned, i.e., the current could not recover fully after the NO_2 gas was shut off. With the contact treatment, on the other hand, this poisoning effect was completely eliminated, suggesting that the single-crystal nanobelt itself was not poisoned but a poor contact between the nanobelt and the Pt electrode could still be poisoned. This finding suggests that the slow recovery observed in the bunch of nanobelts tested in the earlier work was due to poisoning either at the poor contacts between the nanobelts and the electrodes or at the interfaces between connecting nanobelts in the bunch of nanobelts. The elimination of such poisoning is essential, as it allows for high sensor stability and repeatability, the lack of which has prevented the wide use of metal oxide sensors.

It was recently reported that gas sensors based on heated carbon nanotube (CNT) films were highly sensitive but showed sensor poisoning.[11] Such poisoning was likely due to the presence of a large amount of junctions between interconnected CNTs in the CNT film. Although the CNT film sensor could be refreshed upon ultraviolet (UV) exposure[12] or with the use of a gate voltage,[11] these interventions should be avoided in an automated sensor instrument for continuous monitoring.

We have also tested another as-assembled nanobelt sensor consisting of a single nanobelt with diluted DMMP gas obtained from a permeation tube containing liquid phase of DMMP. Figure 3 shows the sensor response to DMMP gas balanced with air when the device was Joule-heated to 500 °C. The current through the nanobelt increased for about 5% and 3%, respectively, in respond to the 78 and 53 ppb DMMP diluted in air. This sensitivity can potentially be enhanced to sub-ppb level by doping the nanobelt with CaO, a catalytic additive for increasing the sensitivity of metal oxide sensors for DMMP detection.[13] In this regard, an ion implantation method has been developed to dope metal oxide nanobelts with manganese (Mn) to tune its electrical and magnetic properties.[14] Most importantly, in contrast with thin film metal oxide sensors for DMMP detection,[15] the as-

assembled nanobelt sensor did not show any poisoning effect upon exposure to DMMP and the current recovered quickly as DMMP was shut off.

These experiments show that low-power, miniaturized gas sensors can be fabricated by assembling "bottom-up" synthesized metal oxide nanobelts with "top-down" fabricated microelectromechanical systems (MEMS) devices. The integration of the two fabrication methods could be a viable approach for large-scale manufacturing of well-organized sensor arrays based on different nanostructures, e.g., CNTs,[16,17] Si nanowires[18] and metal oxide nanobelts, with the complex functionality (such as integrated thermal control) comparable to that of MEMS sensors. It has recently been shown that large-scale vertically aligned metal oxide nanowire arrays can be grown from patterned catalyst.[19] Future advancements in directed growth and directed assembly of nanostructures on MEMS[20] will likely allow for the fabrication of selective gas sensor arrays consisting of functionalized metal oxide nanobelts integrated with a MEMS platform that consists of a microchromatography column and preconcentrator for gas separation and preconcentration. Alternatively, the selectivity can also be obtained with the use of a pattern recognition approach, where an array of sensors made of different metal oxides with different catalytic additives generates a distinct response pattern for a gas species or mixture.

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