Carbon Monoxide Plume Detection with Nanowire-Based Sensors Mounted on an Unmanned Ground Vehicle

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Summary

Two trace chemical vapor sensors, *Si*licon *N*anowires in a *V*ertical *A*rray with a *POR*ous electrode (SiN-VAPOR) [1], and disordered ruthenium oxide (RuO_x) nanoskins coated around silicon dioxide micron/submicron fibers in glass paper [2] have been developed for carbon monoxide sensing. These low-power sensors respond by electrical conductivity changes in the nanowires or their coatings. In laboratory conditions, these sensors demonstrate high sensitivity to carbon monoxide. We also demonstrate plume detection in less-controlled environments. Both sensors were mounted on a semi-autonomous Pioneer 3-AT Unmanned Ground Vehicle (UGV) to validate the technologies for plume detection in real-world environments. The RuO_x nanoskin–based sensor responded consistently as the UGV entered a CO plume estimated at 6 ppm and decreased after passing through the plume.

Background

Small, low-power sensors are needed for detection of hazardous chemicals such as carbon monoxide. For example, a sensor that can be mounted on a mobile platform and provide real-time response to hazardous conditions is needed for applications such as firefighting.

Nanostructure-based sensors with relatively high sensitivity, low power, and fast response have shown great promise under laboratory conditions, but few have transitioned from laboratory curiosities to field tests and prototypes. The failure of nanostructure-based sensors to transition out of the laboratory has largely been due to poor signal-to-noise ratios, where shot noise and 1/f noise are of greater consequence at the nanoscale. Poor recovery, low duty cycles, interference from humidity, and lack of proper testing and understanding of field conditions and deployment platforms are also problems.

The Naval Research Laboratory (NRL) Chemistry Division has been developing a sensor technology, known as Silicon Nanowires in a Vertical Array with a Porous Electrode (SiN-VAPOR), that demonstrates extremely high sensitivity to target analytes in laboratory conditions, and that addresses many of the issues that have hindered the transition of nanostructure-based sensor technologies to the field. In addition, we have developed a promising carbon monoxide sensor consisting of a disordered ruthenium oxide (RuO_x) nanoskin coated around silicon dioxide (SiO₂) micron/submicron fibers in glass paper. The goal of this project was to combine the selectivity of the RuO_x with the SiN-VAPOR sensor.

Sensing methods

Researchers at the NRL are investigating how to enhance the selectivity of the SiN-VAPOR and related sensor technologies. One approach is to coat the silicon nanowires of the SiN-VAPOR architecture with a nanometers-thin layer (i.e., a nanoskin) of a metal oxide selective to the desired analyte. Nanostructure-based sensors using RuO_x nanoskins show promise for selective detection of fire gases such as carbon monoxide (CO) at a reduced operating temperature, and thus with a reduced power budget. We developed a simpler, two-dimensional CO sensor, based on a paper of silica fibers coated with RuO_x nanoskins, to elucidate the sensing behavior without the complication of conductivity changes in the Si nanowires comprising the SiN-VAPOR sensor.

The 2–3 nm–thick RuO_x coating is X-ray amorphous as deposited and crystallizes at relatively low temperatures (~250°C). Crystallization changes the surface chemistry and electrical properties of the

nanoskins making them less desirable as a sensor. Therefore, both the pre-operation annealing temperature and the operating temperature are important parameters to be monitored for optimal sensor performance.

Results

Using the RuO_x-coated SiO₂ fiber paper (RuO_x@SiO₂ paper) as the chemiresistive sensor, the effects of annealing and operating temperature on the CO responsivity of the modified papers were investigated. The ruthenia was more responsive when pre-annealed at 100°C, but less responsive when annealed to 150°C. The sensors were more sensitive to CO when operated at 100°C vs. 50°C. The response to CO is shown in Figure 1, along with a photograph of the RuO_x@SiO₂ paper and an SEM image of RuO_x-coated Si nanowires. The sensor was mounted on a UGV and driven through a plume of CO. The sensor response correlated to 6 ppm CO is shown in Figure 2.



Figure 1. Response of RuO_x coated SiO_2 papers, annealed at 100°C for CO at 100 and 50 ppm. The SEM images show Si nanopillars coated with a RuO_x nanoskin.



Figure 2. Detection of a 6 ppm CO plume with a $RuO_x@SiO_2$ paper-based sensor mounted on a semiautonomous ground cart.

References

[1] C. R. Field, H. J. In, N. J. Begue, P. E. Pehrsson, *Analytical Chemistry*, 83, 4724 (2011)
[2] C. N. Chervin, A. M. Lubers, K. A.Pettigrew, J. W. Long, M. A. Westgate, J. J.Fontanella, D. R. Rolison, *Nano Letters* 9, 2316 (2009)