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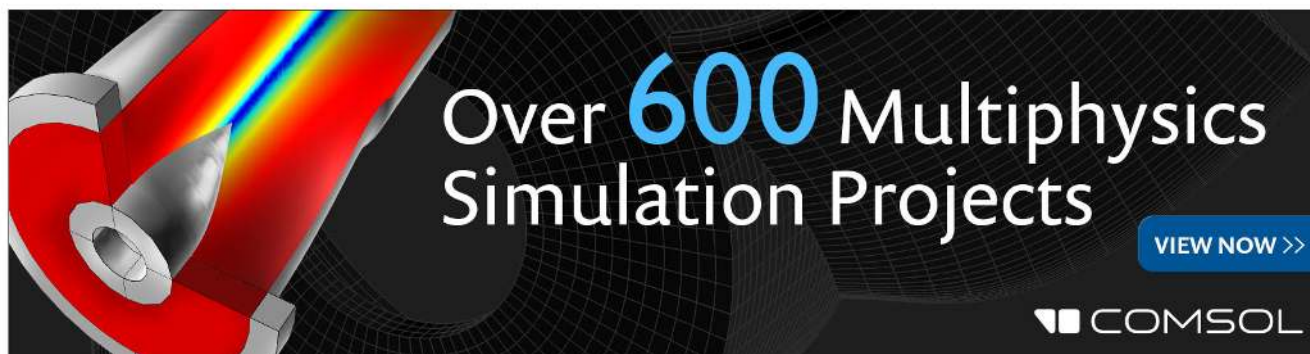Detection of organic vapors by graphene films functionalized with metallic nanoparticles
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Room temperature detection of NO₂ using InSb nanowire

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Room temperature detection of NO₂ down to one part-per-million (ppm) using single crystalline n-type InSb nanowires (NWs) chemiresistive gas sensor is presented. These sensors were synthesized and fabricated by the combination of chemical vapor deposition and dielectrophoresis alignment techniques. The sensor devices showed an increase in resistance upon exposure to successive increments of NO₂ concentration up to 10 ppm. The reduction in conductance of n-type InSb NWs when exposed to NO₂ is made possible due to the charge transfer from the InSb NW surface to the adsorbed electron acceptor NO₂ molecules. The demonstrated results suggest InSb NW as a promising candidate in sensing applications as well as being environmental friendly over existing arsenic and/or phosphorous-based III-V NW sensors. © *2011 American Institute of Physics*. [doi:10.1063/1.3614544]

Detection of nitrogen dioxide (NO₂) in the environment has been considered important because of its effect on human health. Thus, continuous efforts have been made to develop nanostructured solid-state gas sensors due to the fact that they possess some unique material properties along with their high surface-to-volume ratio.[1–3] In the last few years, solid-state chemiresistive sensors fabricated from one-dimensional (1D) nanostructures such as carbon nanotube (CNT), tin oxide (SnO₂), indium tin oxide (ITO), indium oxide (In₂O₃), and zinc oxide (ZnO) have been reported showing their surface sensitivity to various adsorbed gaseous molecules down to parts-per-billion (ppb) level.[4–8]

Furthermore, III-V compound semiconductor nanowires (NWs) such as InAs, GaAs, InP, GaP, and InSb have been investigated as building block materials in nanoelectronic devices because of their high electronic transfer characteristic with low leakage currents as well as the existence of an electron surface accumulation layer that leads to high surface sensitivity towards various gaseous species or biomolecules.[9–13] In fact, the label-free molecular detection mechanism of those NWs devices has been made possible utilizing the direct charge transfer on the surface by the adsorbed molecules. However, among the III-V semiconductor materials studied so far, InSb has narrowest direct bandgap (0.18 eV at 300 K) and the largest bulk electron mobility ($\sim 7.7 \times 10^4$ cm² V⁻¹ s⁻¹) that make it a promising semiconductor material in nanoelectronics.[14,15] Moreover, InSb is environmental friendly over As and/or P containing semiconductor materials. However, despite its superior material properties, no reports on the sensing properties of InSb NWs gas sensors have been published.

In this communication, we report a chemiresistive NO₂ gas sensor using chemical vapor deposition (CVD) grown n-type InSb NWs. NO₂ is a widely known toxic gas and the permissible exposure limit (PEL) as defined by Occupational Safety and Health Administration (OSHA) stands at 5 ppm.

Fabricated InSb NWs sensor devices showed promising response in sensing NO₂ down to 1 ppm at room temperature.

Single crystalline n-type InSb NWs having an average diameter of 10-25 nm were synthesized using chemical vapor deposition technique, as described previously (see supplementary Fig. S1).[16] Briefly, the native oxide on the InSb substrate was removed by chemical etching in aqueous HCl (10%) solution and dried by argon blowing. Gold nanoparticles (60 nm diameter) decorated InSb substrate (NWs growth substrate) and InSb source powder were placed inside a 10 mm diameter quartz tube mounted in a 5 cm diameter quartz tube furnace such that the powder source was at 550 °C while the NWs growth substrate was at 400 °C. The InSb NWs growth was performed for 1 h in flowing argon (100 sccm) and hydrogen (100 sccm) atmosphere.

For InSb NWs sensor device fabrication, the as-grown InSb NWs were suspended in water by brief sonication of the growth substrate and the dispersed nanowires were aligned across a pair of source-drain gold electrodes with 3 µm channel length defined on SiO₂ (300 nm)/Si substrate using photolithography as reported previously,[17] by ac dielectrophoresis (DEP) technique as follows.[18] In brief, a 0.1 µl drop of NWs suspension was placed between the electrodes using micropipette, followed by applying an ac electric field (0.36V_RMS) at 4 MHz frequency across the electrodes. The aligned NWs were then annealed at 300 °C for an hour in flowing 95% Ar + 5% H₂ atmosphere to minimize the contact resistance between the NWs and metal electrodes. The annealing step improved contact between NWs and metal electrodes as evident by the decrease in the device resistance from ~900kΩ to 10-110kΩ after DEP aligning and annealing, respectively. This is due to the removal of the water vapor from the interface between NW and metal electrode. Scanning electron microscopy (SEM) image of assembled devices showed that there were multiple InSb NWs aligned between the gold electrodes (Fig. 1(a)), and most of the NWs were aligned and suspended between the electrodes (Fig. 1(b)). The suspended NWs would be beneficial for the better response in our experimental

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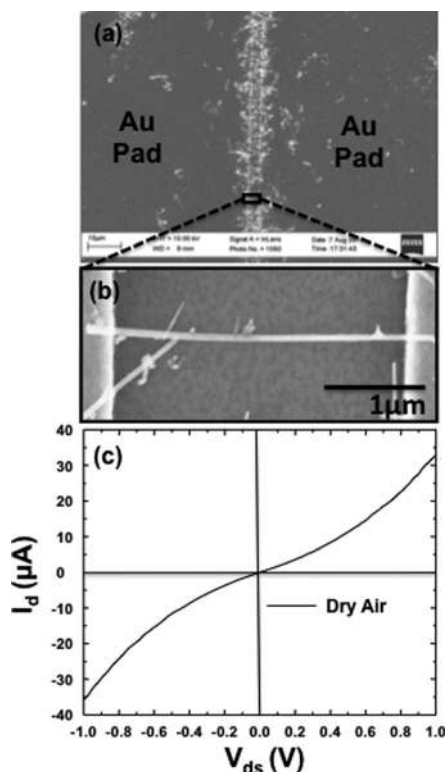b)Electronic mail: adani@engr.ucr.edu.

FIG. 1. (a) SEM image of the aligned InSb NWs bridging the source-drain electrodes after ac dielectrophoresis alignment. (b) Enlarged SEM image of an individual suspended InSb NW between electrodes. (c) Two terminal source-drain current-voltage (I_{ds}–V_{ds}) characteristic curve of the InSb NWs sensor device exposed to dry air.

conditions due to their maximum surface exposure to flowing analyte gas molecules. Electrical characterization (I_{ds}–V_{ds} curve) of the assembled device (Fig. 1(c)) showed almost symmetrical nonlinear portions in at the high bias regions revealing the existence of Schottky barriers in the system, a frequently observed phenomenon at the metal-semiconductor interfaces.[19] To ensure that the resulting resistance modulation during sensing was distributed in the nanowire itself, in this work, the resistance of sensor was calculated from the slope of the I_{ds}–V_{ds} curve from a low bias region (-0.5 to $+0.5$ V), where the I_{ds}–V_{ds} response was linear.

To evaluate the performance of InSb NW device as chemiresistor gas sensor, the electrodes with aligned nanowires were connected to a chip holder by wire bonding and placed in a 1.3 cm^3 glass chamber with inlet and outlet ports (see supplementary Fig. S2).[26] Dry air or air/NO$_2$ mixtures at a total flow rate of 200 sccm were flowed into the glass chamber using mass flow controllers (MFCs). The sensor arrangement was subjected to 0.5 V potential corresponding to the potential window (-0.5 to $+0.5$ V) in the linear region of the I_d–V_{ds} characteristic curves of the sensor in Fig. 1(c) and the resistance of the sensor was determined continuously using a dual channel Keithley Source Meter (Model 2363A). A custom Labview computer program was developed to control the mass flow meters and to monitor the resistance of the nanowire. The sensing experiment was started by first purging the glass chamber with dry air for 200 min to stabilize the resistance of the sensor, followed by increasing NO$_2$ concentration in air every 50 min with an interval of 50 min recovery in air between two successive NO$_2$ exposures. Figure 2(a) shows normalized change in resistance

[{$(R - R_0)/R_0$}, where R and R_0 are the resistances in analyte gas and air, respectively] as a function of time from a sensor device operating at room temperature. As expected, the resistance of the device increased with increasing NO$_2$ concentration. This is attributed to NO$_2$ being a strong electron acceptor, which would reduce the electron density in the surface of the n-type InSb NWs by charge transfer from InSb NW surface to the adsorbed NO$_2$ gas molecules. However, no response to gas exposure was observed for devices without nanowires. This result is comparable with previously reported III-V InAs semiconductor NW gas sensors.[12,13] The sensor response, after 50 min exposure, was a linear function of NO$_2$ concentration from 1 to 10 ppm (Fig. 2(b)). The sensitivity, determined from the slope, was 1.05% per ppm NO$_2$, and a detection limit of 1 ppm NO$_2$ (2.5%) could be easily achieved with a signal-to-noise ratio of 4.15. This result is comparable to recently reported CNTs (20 μm)/reduced graphene hybrid NO$_2$ sensor devices which showed a response of about 3.5% at 1 ppm NO$_2$ exposure.[20] Moreover, we also demonstrated the sensing property of the n-type InSb NWs sensor devices towards H$_2$O vapor (see supplementary Fig. S3).[26] As expected, the resistance value of the InSb sensors decreased with increasing H$_2$O vapor contents confirming the role of H$_2$O molecules as an electron donor for III-V semiconductor, which would increase the carrier density in the InSb NWs. This result is in accordance with recently reported n-type InAs NW sensors that showed an increase in conductance to H$_2$O vapor exposures.[12] Thus, the fabricated InSb NWs sensors may successfully be used to detect some other electron-donating as well as electron-withdrawing species.

Figure 2(a) shows that while the response time of the InSb NW sensor decreased, the recovery rate on the other
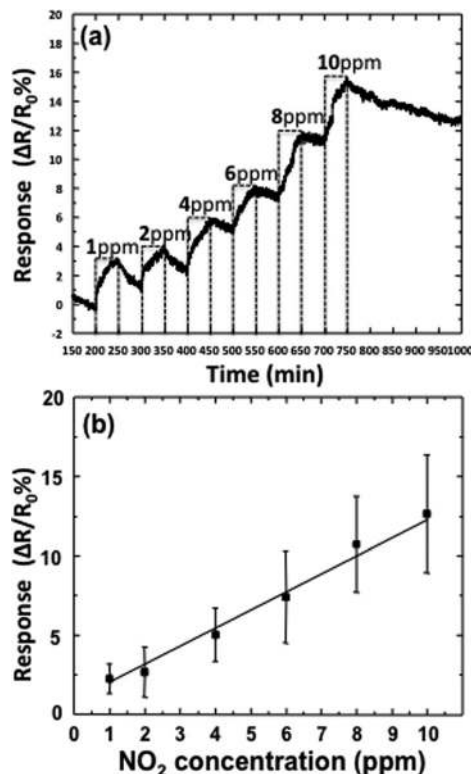

FIG. 2. (a) Dynamic response ($\Delta R/R_0$%) and (b) calibration curve for NO$_2$ of InSb sensors to varying concentrations of NO$_2$ in dry air (the data point is an average of the response of four sensors after 50 min exposure and the error bar represents ± 1 S.D.).

hand was slower for increasing NO_2 concentration. A similar slow recovery of NO_2 gas sensors has been observed previously.[20,21] Exposing the sensor to UV light or high temperature could accelerate the recovery rate by desorption of NO_2 molecules.[7,20] We investigated the effect of temperature on the extent of recovery and recovery time of the InSb NW sensor to 4 ppm of NO_2 in dry air (Fig. 3(a)). As shown in the figure, a faster recovery and an improved extent of recovery was observed at higher temperature attributed to an accelerated desorption of NO_2 molecules. In addition, the response time, defined as the time required reaching 90% of the maximum resistance change, decreased from $\sim$50 min at room temperature to 13 min and 12 min at 50 °C and 100 °C, respectively.

In several works, on both organic and inorganic semiconductor film based sensors, the kinetics of sensor response were found to follow the Elovich chemisorption model

$$dN/dt = a\exp(-bN), \qquad (1)$$

where a and b are constants and N is the amount of adsorbed NO_2 molecules on the semiconductor surface.[22,23] Assuming that the modulation of sensor conductance upon exposure to analyte gas is proportional to the amount of molecules adsorbed on the sensor surface, then according to Elovich equation, a plot of conductance change against log (t) should exhibit a linear relationship. A good linear agreement between the normalized resistance change and log (t) for the InSb NW sensor exposed to 4 ppm NO_2 for both room temperature and 100 °C (Fig. 3(b)) thus confirmed that the sensor response was driven by the adsorption of NO_2 molecules at the InSb NW surface and the adsorption increased with time due to an increase in NWs surface coverage by NO_2 molecules.[24,25] Moreover, these profiles also confirmed the dependence of this process on the temperature of the InSb

NWs surface; i.e., as temperature increases up to 100 °C, the response delay time was reduced.

In summary, we investigated the sensing property of n-type single crystalline InSb NWs for NO_2. When operated at room temperature, the sensor was able to detect NO_2 down to 1 ppm, which is five times lower than OSHA permissible limit of 5 ppm. The sensitivity of the sensors corresponding to the reduction of carrier density of n-type InSb NWs was related to the variation of sensor resistances with variation in concentrations of NO_2 exposures. We are currently investigating the functionalization of InSb NWs to increase the sensitivity towards other gaseous species as well as different biomolecules. Our demonstrated results provide InSb NW as an attractive sensor material on the platform of other III-V semiconductors.
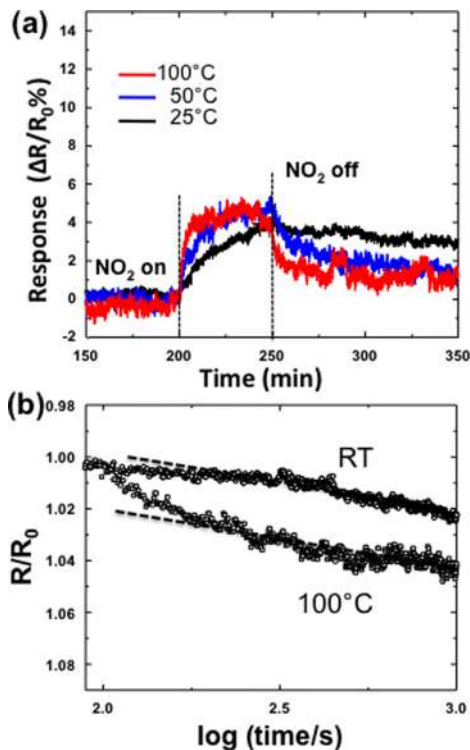
FIG. 3. (Color online) (a) Response and corresponding (b) Elovich plots of relative resistance variation of InSb NWs sensor to 4 ppm NO_2 at different temperatures.

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