Electrically controlled nanowire-based chemical sensors

Jia Grace Lu

We have built a highly sensitive ZnO nanowire field-effect sensor with electrically controlled sensitivity, refreshability, and distinguishability.

The detection of hazardous gases (such as NO₂, CO, NH₃, H₂, H₂S, CH₄, etc.) in the environment is of paramount importance for personal health and public security: especially in the automotive, aerospace, semiconductor, utility, and power industries. For such detection, solid state sensors are among the most useful owing to their reliability, life expectancy, and low cost. At the same time, metal oxides have remarkable properties, such as high sensitivity to changes in a chemical environment. With the appropriate doping, structure processing, and operating temperature, they can be manufactured into commercial sensors. The operating principle of metal-oxide devices is based on the transduction of adsorbed chemicals on the sensor surface with a corresponding change in the electrical conductance. The challenge is to build sensors not only with enhanced sensitivity, but also with the ability to detect specific chemicals in a complex environment (selectivity), and to be quickly ‘reset’ for the next sensing cycle (refreshability). With the advent of nanotechnology, nanostructured materials with novel characteristics seem set to address these challenges.

An assortment of quasi-one-dimensional (Q1D) metal oxides (such as nanowires, nanobelts, and nanotubes) have been synthesized using bottom-up methods. Such structures with a high aspect ratio (i.e. size confinement in two coordinates) have better crystallinity, consume less power, and yield higher integration densities. Due to a large surface-to-volume ratio and a Debye length (the distance over which a local electric field affects the distribution of free charge carriers) comparable to the size, they exhibit superior sensitivity (at room temperature) to surface chemical processes in comparison with their bulk and thin film counterparts. When they are configured as field-effect transistors (FETs), the applied gate potential can effectively control surface processes. Furthermore, the diffusion time of carriers to the surface is significantly reduced, leading to a faster recovery response.

In order to build high performance sensors, our group has investigated devices based on zinc oxide (ZnO) nanowires configured as FETs. Single crystalline nanowires (with a typical diameter of about 50nm) were synthesized via a chemical vapor deposition method. Figure 1 illustrates an atomic-force-microscope (AFM) image of a ZnO nanowire FET with a schematic of the measurement circuit. Electrical measurements show that the ZnO nanowires are n-type semiconductors. The measured room-temperature electron concentration is of the order of \(10^{19} \text{cm}^{-3}\), and the electron mobility of these nanowires ranges from 20 to 100 \text{cm}^2/\text{Vs}.

The metal oxide sensing mechanism originates from the charge transfer between the semiconductor and the chemical species adsorbed at the surface oxygen-vacancy sites. The relative change of conductance after exposure to a target gas determines the sensitivity. For example, the conductance of ZnO

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Figure 2. Nanowire sensing response to NO$_2$ and the conductance recovery process induced by a large negative gate voltage pulse.

decreases with the introduction of NO$_2$. At room temperature, with the ZnO in the form of a nanowire, more than 50% of the conductance change was observed under an exposure of 0.6ppm NO$_2$. In comparison, doped ZnO thin films achieved less than 2% conductance change when exposed to 1.5ppm NO$_2$. This demonstrates a high potential for nanowire sensors with superior sensitivity. Moreover, sensitivity can be tuned by exploiting a transverse electric field induced by the gate in the FET configuration. Above a gate threshold (the voltage at which the electrons are depleted in the channel), the sensitivity decreases with increasing gate voltage. This implies that the gate voltage can be used as a knob to adjust the sensitivity range.

More importantly, we discovered that the gate potential can electrically desorb the absorbed gas molecules. Chemical sensing at room temperature is generally not easily reversible because the available thermal energy is usually lower than the activation energy for desorption. This results in a long recovery time. One common method for refreshing sensors is via ultraviolet (UV) illumination, but this increases the complexity of the sensor design, and the recovery time can be fairly long. We developed a gate-refreshing mechanism to improve this situation; as shown in Figure 2, the conductance of a nanowire can be electrically recovered by applying a negative gate voltage much larger than the threshold voltage. This reduces the chemisorption rate, and the hole migration to the surface (driven by the negative field) leads to a discharge of chemisorbed species. For instance, both NO$_2$ and NH$_3$ cause a conductance reduction at room temperature. However, the gate voltage required to desorb the NH$_3$ molecules is significantly lower than for NO$_2$. Under the same voltage pulse duration, the minimum refresh voltage is concentration dependent (see Figure 3). In addition, the time domain response for NO$_2$ and NH$_3$ during the refresh process shows a clear difference, and the recovery rate for NH$_3$ is twice as fast as that of NO$_2$. This distinguishability illustrates the feasibility of identifying a specific chemical gas.

In summary, we present a ZnO nanowire field-effect chemical sensor, demonstrating a self-integrated device with gate tunable sensitivity, gate refreshability, and gate controlled distinguishability. Even though there has been considerable effort in this field, much remains to be elucidated and developed. Very little work has been done in modeling and simulation to understand the surface and interfacial processes at the atomic level. Combining theoretical models with experimental investigations will enable new research and guide the design of sensors with optimized properties. Ultimately, we envision a smart sensor array system that integrates the sensing elements with signal processing on a single chip. This kind of approach—with multi-component chemical analysis integrated with pattern recognition—should help meet the challenge of selectivity.

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References