SEMICONDUCTING METAL-OXIDE NANOWIRE GAS SENSORS

A. JAMES CLARK SCHOOL OF ENGINEERING

NIST National Institute of Standards and Technology

Co-Laboratory for Nanoparticle Based Manufacturing & Metrology

Lab Director: Dr. Michael R. Zachariah mrz@umd.edu

Lab-Affiliated Faculty: Dr. George Mulholland georgewm@umd.edu

Researchers: Prahalad M. Parthangal, Richard E. Cavicchi and Michael R. Zachariah

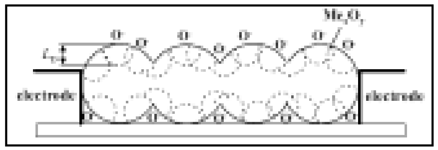
Funding Agency
NIST

BACKGROUND

Semiconducting metal oxides such as tin oxide (SnO_2), zinc oxide (ZnO), and titanium oxide (TiO_2) have been widely used as active materials in solid-state gas sensing devices. Adsorption of gas molecules on the surface of a metal-oxide semiconductor causes a significant change in the electrical conductance of the material, which is the operating principle of traditional solid-state gas sensors. While several different approaches to gas detection are available, metal oxide sensors remain widely used because of their low cost, versatility and longevity. In particular, nanostructured materials possessing very high surface to volume ratios are of great interest since the solid state sensing mechanism is governed primarily by the available surface area.

GAS SENSING MECHANISM

Adsorption of gas molecules (typically oxygen from the surrounding air) onto a metal-oxide sensor surface creates new surface states. When the sensor surface is exposed to a test-gas, the surface concentration of adsorbed oxygen changes, thereby modulating the conductivity of the sensor.



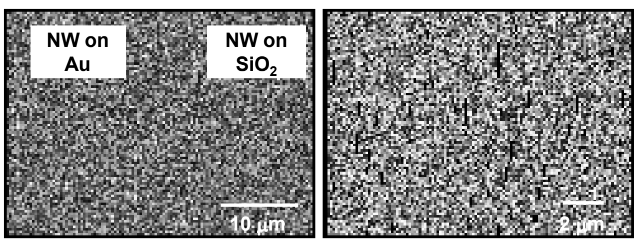
Reducing test gases such as hydrogen (H_2) and methanol (CH_3OH) cause a reduction in adsorbed oxygen, leading to a drop in sensor resistance. E.g. $CH_3OH + O^- \rightarrow HCHO + H_2O + e$

Oxidizing test gases such as nitrous oxides (NO/NO_2) and ozone (O_3) on the other hand lead to an increased sensor resistance. E.g. $NO_2 + e \rightarrow NO_2^-$

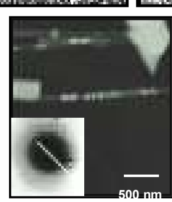
ZINC OXIDE NANOWIRE SYNTHESIS

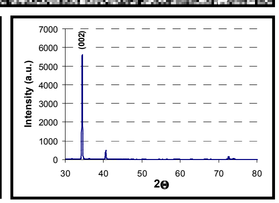
Zinc oxide (ZnO) is a wide-bandgap semiconductor (E_g = 3.37 eV) having enormous potential in the development of new electronic and photonic devices. ZnO nanowires (NW) provide an interesting morphology for gas sensors since their high aspect ratios (L/D) account for superior surface to volume ratios. We have synthesized nanowire arrays of ZnO on silicon dioxide (SiO_2) substrates containing catalytic layers of gold (Au) through a direct thermal evaporation of Zn powders within a horizontal tube furnace at 550 °C.

NW on Au are vertically aligned while the NW on SiO_2 are more randomly oriented. The NW have widths between 60-80 nm and lengths between 5-10 µm. Diffraction analyses indicate that the NW are single crystalline and grow along the c-axis.



The NW on Au follow a catalytic vapor-liquid-solid (VLS) growth mechanism with Au providing nucleation sites for the ZnO NW to grow. The NW on SiO_2 follow a self-catalytic vapor-solid (VS) mechanism where Zn and its suboxides condense on the substrate and act as nucleation sites for NW growth.

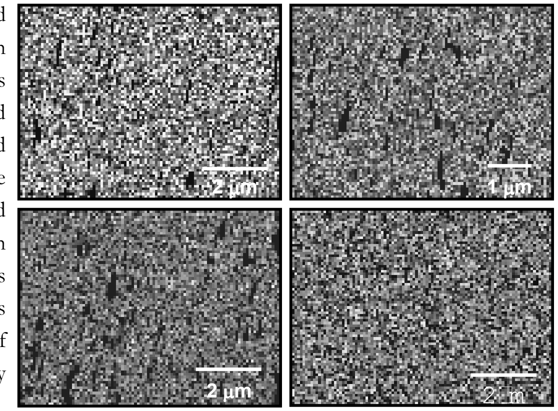




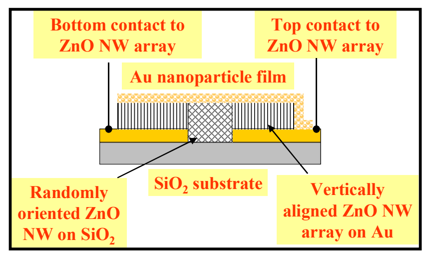
CONNECTING NANOWIRES WITH NANOPARTICLES

Despite significant advances in NW growth techniques and device descriptions, non-destructive techniques for achieving contact electrodes to NW arrays have not been realized before. We developed a novel, generic approach of connecting NW arrays with Au nanoparticles attached exclusively to NW tips.

The electric field enhancements around the sharp tips of NWs combined with high aspect ratios was exploited in this approach. Au nanoparticles, generated though an aerosol spray pyrolysis method and charged with a unipolar charger, were deposited onto ZnO NW arrays placed within an electrostatic precipitator. A high electric field of opposite polarity drives the particle deposition onto the NW tips forming a conductive film over a period of time. Such an approach enables the study of NW arrays as-grown.

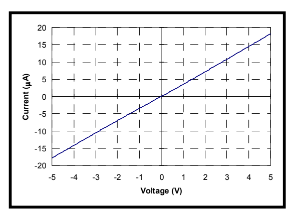


GAS SENSOR DESIGN AND MEASUREMENTS

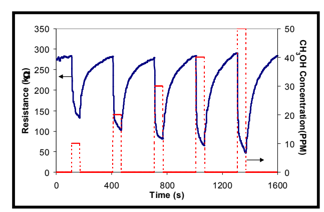


The Au nanoparticle film was deposited such that it acted as a continuous top contact electrode to the NW array while the Au catalyst layer acted as the bottom electrode. The electrodes were generally robust and stable even at temperatures around 350 °C. This ZnO NW based gas sensor was found to be sensitive to very low concentrations (10-50 ppm) of both CH_3OH and NO_x.

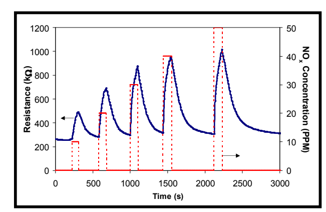
I-V Characteristics



Responses to CH_3OH



Responses to NO_x



CONCLUSIONS

An original, generic approach of connecting ZnO NW arrays with Au nanoparticles was successfully developed. A gas sensor based on this nano-assembly approach was fabricated and observed to be highly sensitive to both reducing and oxidizing gases. This approach may be suitable for the design of electrically driven optical devices based on nanowires such as nano-lasers and LEDs.