Recent Trends in the Fabrication, Functionalization and Characterization of Metal Oxide Nanowire Gas Sensors

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Abstract: Due to strong interdependence of the electron transport and surface processes in quasi 1-D metal oxide nanostructures, chemiresistors and field effect transistors (FETs) based on nanowires perform excellently as sensing elements and may be able to compete with or even substitute for traditional thin film sensors in the field of solid state sensorics. Namely, applications requiring a stable, reproducible sensing element of small size with sensitive performance will benefit from this new platform. In this report, a few recent trends in the fabrication, functionalization and characterization of quasi 1-D metal oxide nanowire sensors are reviewed.

Keywords: metal oxide nanowires, chemical sensors, catalysis, field effect transistor, spectromicroscopy, surface science;

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1. Introduction

1.1 Motivation for research

Recently tightened controls on detecting requirements for environmental pollutants, explosive agents, and toxic gases along with advancements in nanotechnology has triggered the search for new nanoscopic active elements which would respond to an analyte more selectively, sensitively and stably (so-called "3S" requirements) in comparison with already available sensing platforms. Considering the moiety of *conductometric* sensors, modern nanotechnology is able to offer a number of prospective sensing elements including quasi-1D semiconducting metal oxides, carbon nanotubes, and nano porous materials. In particular, quasi-1D metal oxide sensing elements are a natural choice for conductometric nanosensors because one can draw from an extensive knowledge base on traditionally well-studied and widely-used nanostructured thin oxide films.

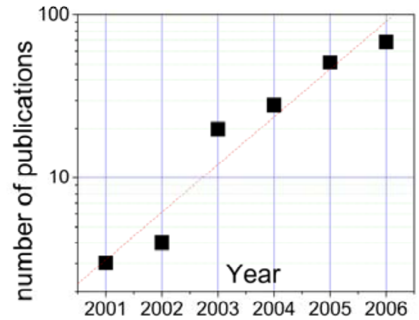

Figure 1 Publication statistics per year on *oxide nanowires sensors* (ISI Web of Science)

Since the publication of a few fundamental demonstrations[1-6] of detecting a variety of chemical and bio-agents using semiconducting 1D oxides, this area has been experiencing significant growth in the past six years (see Fig.1) and it is not yet clear whether it will reach saturation soon. The performance of gas sensors composed out of pristine quasi-1D metal oxide nanowires (both individual, chains and mats) measuring 20-500 nm in diameter have already been tested by many groups and the number of publications on this issue is currently approaching 200 (see recent reviews[7-13] and references therein). Given that the fabrication and performance aspects of these newly emerging sensing elements have been topically reviewed by a number of authors, this report will focus on a few emerging approaches to the fabrication, functionalization and characterization of 1D metal oxide conductometric sensors, which, in our opinion, will contribute to this field's further development.

1.2 Features which make metal oxide nanowires prospective chemiresistors and chemi-FET chemical sensors

Quasi-1D metal oxides possess several important properties which make them particularly attractive for use in chemical sensing. They are:

A. Their generically high surface to bulk ratio (S/B). This characteristic implies that a significant number of atoms are exposed on the surface and therefore available for surface reactions with analyte molecules. It is favorable in gas sensing to increase this ratio, and it is the largest for the thin nanobelts and tubular, porous 1D nanostructures.

B. Many of the surface-gas interactions (e.g. chemisorption and other chemical reactions) proceed via electron (or, in the case of photo-assisted sensing, exciton) exchange with the nanostructure's bulk. The delivery of these "reactive" species from the bulk to the surface is particularly easy if the nanostructure's effective diameter falls at or below 10 nm (i.e., comparable with the mean free paths of these electronic excitations). Nanostructures of this size also have an important implication for nanosensors where low temperature is required. As an example, room temperature photo-assisted sensing[2,14] will be particularly pronounced when the nanostructure's diameter is comparable to the mean free path for photo-excited carriers.

C. As in the case of macroscopic semiconductors, the Debye length L_D is a measure of the electronic "cross-talk" between the surface processes and bulk electronic structure. When a semiconductor oxide is moderately doped (10^{17}-10^{18} cm^{-3}), L_D falls into the 10-100 nm range. For nanostructures with radiuses comparable to the L_D this implies that surface band bending due to ionosorbed chemical or biological agents will comprise the entire volume of the nanostructure. Therefore the resultant electron depletion/accumulation due to adsorption/desorption events will drastically influence the conductivity of the nanostructure.

D. In principle, nanoparticles and clusters as sensing elements offer the same advantages as described above[15]. However, 1D nanostructures offer a crucial component making them an almost ideal choice for conductometric sensors. Namely, due to their 1D morphology, nanowires sensors possess a structurally and compositionally well-defined conducting channel measuring microns long, thus making these nanostructures easily integrated with the existing microfabrication technology. In addition, the same conducting channel can be used not only as an antenna for the surface processes but also in the reverse manner: as an active control over the surface reactivity [16,17].

E. Finally, thanks to recent progress in nanotechnology, fine control over the crystallinity, faceting, morphology, composition, and doping level of these quasi-1D sensing elements can be achieved and potentially allow for unprecedented level in their stability, reproducibility and modeling.

1.3 Operating principles of conductometric metal oxide nanowire sensors

The operating principles of a nanowire chemiresistor and chemi-FET are basically the same as those of their macroscopic counterparts (see for example [18,19]). Namely, one can define two major nanosensor functionalities:

(i) *receptor function* which defines how actively and target-specifically the surface of the nanostructure interacts with the intended molecules. This function depends on the availability and nature of reaction (adsorption) sites and the specifics of the nanowire surface chemistry. The receptor function can usually be tuned via selection of the oxide material, temperature and/or via functionalizing the surface with catalyst or target-specific "key-lock" molecules.

(ii) *transduction function* which determines the mechanism of converting the surface interaction event into an electrical signal. For simple adsorption/desorption events which proceed by a charge transfer between the target molecule and the moderately-doped semiconducting nanowire's surface, the modulation of the potential barriers along the radius of the nanowire occurs due to the charging (the so-called "chemical gating") of the near surface layer.

In addition to the aforementioned major factors, variables such as contact resistance, substrate effects and uncontrolled impurities can play a significant role in the overall performance of these devices [20-22].

5. Conclusions and outlook

The performance of metal oxide (MOX) nanowire chemiresistors and chemi-FETs is promising for their use as a new platform for the next generation of miniature gas sensors and electronic noses. While the sensitivity and stability of the nanowire sensors has been demonstrated to be excellent, the selectivity still remains a challenge. At least two approaches can be envisioned in this regard: (i) to create more sophisticated arrays of nanowire sensing elements to improve the recognition function of the device and (ii) to create much simpler "alarming" sensors exclusively specific to certain classes of reactants. The latter is a promising option for Pt/MOX or Pd/MOX nanowire hydrogen sensors; however, different target gases would require extensive searches for specific catalysts (receptors).

Fundamental research still needs to be conducted on low-dimensional oxide nanostructures to explore the interplay between surface reactions and electron/hole transport. The latter would require the application of new surface-sensitive spectromicroscopy techniques in conjunction with taking transport measurements. Real-world conditions make sensitive transport through the conducting channel susceptible to tiny changes of the electrostatic environment of the neighboring oxide areas and/or contacts. To better understand the influence of these factors on the sensing performance of nanowire devices, an array of environmental AFM- and SEM-based images can be invaluable tools.

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