Metal oxide nanowire chemical sensors: innovation and quality of life

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Metal oxides are emerging as important active materials for applications such as sensors. Recent advances in the preparation of metal oxide materials offer unique possibilities for their integration into devices with new capabilities, for example, wearable/flexible devices, smart textiles for well-being and health monitoring in everyday life, or with innovative sensing architectures such as work function, surface ionization, magnetic, self-heating, and Schottky-based devices. This review presents the author's opinion on innovations and challenges in the field of metal oxide nanowire chemical sensors.

Introduction

Nanotechnology and nanoscience are increasingly attracting attention and investments all over the world. Available literature as well as the Internet does not offer a unique definition for nanotechnology. Nanotechnology operates at the first level of atom and molecule organization, which forms the core and starting point for definition of materials' fundamental and functional properties. Nanotechnology is essential to acquire knowledge of the matter, and nanoscale phenomena hold the promise for fundamentally new applications and to build a first step toward industrial prototyping and commercialization. For this reason, control (at this scale level) is essential to create new, broad and revolutionary technologies and platforms for every area of interest, such as industry, biomedicine, environmental engineering, safety and security, food and water resources quality control, and energy conversion.

In particular, sensors have (and would have) an increasing impact on many aspects of our life: chemical sensors are indeed a required interface to acquire chemical information out of our surroundings in real time. This information may provide control systems with feedback on an incredibly large number of chemical processes: detection of toxic analytes and explosives, alarming systems for gas appliances, security systems to protect workers from chemical hazards, outdoor monitoring, food chain control, health, and wealth monitoring. Moreover, chemical sensors may be spread out and used in networks, to monitor chemical information as a function of location and time, giving a distribution map of harmful and toxic chemicals over large areas during the day. The quality of atmospheric air, such as indoor air, may be monitored and correlated to chronic diseases, for example, getting insights on how to increase health and wealth.

In fact, in Italy (the author's country), the concepts of spirit, mind, body, and wellness accompany everyone's everyday life and have a great meaning. Over the years, this concept has gained more and more value and, at present, it refers not only to the absence of diseases but also to a general condition where spirit, mind, and body, including psychological, mental, and physical health, are considered as a whole.

Unfortunately, in order to be used in real applications, chemical sensors should fulfill stringent requirements depending on the specific purpose and operation conditions (sensing performances in terms of sensitivity, selectivity and response kinetics, and reliability (drift and stability)). These requirements are strictly correlated to the active materials used and that is why materials design is the starting point for the development of new sensors and new gas sensor technologies. Therefore, the impact of material design in the research and development of chemical sensors is fundamental.

On account of these reasons and applications, gas sensor technology is becoming essential in various aspects of our everyday life. Still, advancements in nanotechnology are effectively needed to improve the sustainability of our society and quality of life. This short review article reports the author's personal opinions about

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the key advances that have been made and what is yet to be done in this field.

Chemical sensors

Conductometric chemical sensors based on metal oxide semiconductors have been known since 1954–1962, when the effects of reaction of metal oxides with the surrounding atmosphere were discovered [1–3] and the first commercial gas sensor was developed [4]. Since then these sensors attracted the attention of researchers working on sensors, because of low cost of fabrication, simple preparation and operation, and large number of potential detections and applications together with the possible device miniaturization. The improvement of their sensitivity, selectivity, stability, and speed (i.e. response and recovery rates) remains a challenge. The interaction between gas molecules and active oxide takes place at its surface; therefore, the atoms of the surface are crucial in chemical sensing performances. Nanowires in particular present a high surface-to-volume ratio that provides a way to enhance the effects of surface phenomena (that are at the base of chemical sensing mechanism); moreover, they may be single crystalline and have well-defined crystal orientations, leading to controlled reactions and increased stability. Response dynamics should be faster compared to their polycrystalline counterpart because there is no need for gas diffusion preliminary to surface reaction. Finally, some of the interesting effects that can be exploited in chemical sensing (such as self-heating) exist only for the nanowire morphology.

Innovation is always the key to open new frontiers and boost the scientific and technological progress. Concerning chemical sensors, there are different ways to bring innovations: designing sensors using new transduction mechanism, sensors for the detection of new chemicals, improving the sensitivity of a known active material or lowering the detection limit for a chemical species, developing room-temperature chemical sensors, improving compatibility with large-scale production systems, portability, and wearability. Most of the chemical sensors reported in literature have been designed based on empirical expertise rather than basic knowledge of materials. On the contrary, fundamental studies are crucial to understand gas-sensing mechanism and select the key factors that influence their performances in order to have a secure ground to boost concrete innovations.

Metal oxides have been integrated into functional devices since long time: tin, titanium, tungsten, and zinc oxides have been extensively investigated, especially for chemical sensing, due to their better thermal, chemical, and mechanical stability compared to organic materials. The key features that an ideal sensor should have include operation at room temperature, no need of filters, heating systems or radiation to ease response or recovery dynamics, low detection limits, high sensitivity and selectivity, high reproducibility, fast response and recovery, and low cost. This would be an ideal sensor of course, but some of these features cannot be discarded, if we are looking for a real device.

Recently, flexible/wearable sensors (Fig. 1) have attracted a lot of attention especially due to their potential impacts on the preparation of portable–wearable systems for health and wealth monitoring throughout our entire life. The use of nanomaterials (semiconducting nanowires, metal oxide nanowires, and carbon-based nanomaterials) with high surface-to-volume ratio can allow the achievement of improved sensing performances.

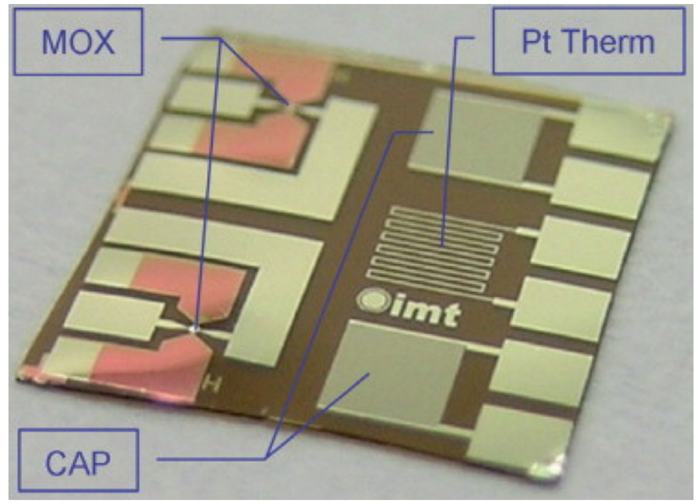

FIGURE 1

Microscope photograph of the multi-sensor platform. Reprinted with permission from Ref [11]. Copyright (2009) by the Elsevier.

Researchers are making efforts to incorporate different sensors into our daily life, using common substrates such as plastic, textile, and paper. The preparation of oxide-based sensors on these transducers is mandatory to develop sensor networks of light, hand-held, portable, consumer devices.

A number of approaches have been reported for the preparation of these devices, with most of them using post-growth integration procedures (see reviews [5,6]). Here we will just briefly discuss some aspects relevant for flexible/wearable chemical sensors. The direct preparation on flexible/wearable substrate has the advantages of easier fabrication processes and low cost. However, the growth of high-quality oxide nanowires on flexible substrates has been difficult primarily due to its thermal requirements to avoid substrate damage. In the case of wearable/flexible substrates, the deposition temperature must be well below the plastic–glass transition or thermal degradation temperature of the substrate. Furthermore, when dealing with solution phase methods there may be restriction on the precursors and solvents. On the other hand, dry or wet techniques may be used to transfer the as-deposited high-quality oxide nanowires from the host substrates to plastic ones.

One of the first methods proposed was the superlattice nanowire pattern transfer (SNAP) [7] approach in 2007 concerning the integration of silicon nanowires into biological and chemical sensors on plastic. Later, other technologies were also reported for the assembly of metal oxide nanowires. The most used methods, and compatible with large-scale production, are contact or roll printing [8], the Langmuir–Blodgett technique [9], and dielectrophoresis [10]. Dielectrophoretic assembly allows a precise positioning with the use of electromagnetic fields between metal contacts, which is in principle compatible with flexible substrates provided the solution does not damage the substrate, and metal contacts are necessary to induce alignments.

Flexible sensors

Most of the studies about flexible/wearable metal oxide sensors do not concern metal oxide nanowires. Indeed, these works still deserve attention because, thanks to the easier integration, research efforts were often devoted to other key issues essential for

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