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Low concentration CO gas sensing properties of hybrid ZnO architecture

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ABSTRACT

ZnO thin film and nanowire morphologies were employed to fabricate CO gas sensors by using radio frequency magnetron sputtering and chemical vapour deposition growth. The sensing properties were measured at CO gas concentration ranging from 10 to 50 ppm at varying operating temperature. The results showed a 5-folded sensitivity and half-reduced response time for the hybrid material based on both thin film and nanowires with respect to thin film only, thus indicating the high potential of morphology tailoring, namely, the surface-to-volume ratio and depletion layer, for the enhancement of ZnO sensing performance.

1. Introduction

ZnO is an n-type semiconducting metal oxide which exhibits remarkable properties such as wide band gap (3.37 eV), great variety of available morphologies (thin film, nanowires, tetrapods etc.), amenability to doping and high chemical stability, beside being highly abundant in nature, low cost and non-toxic [1–3]. Over the last years, it received increased interest for a wide range of applications including gas sensors, optoelectronics, solar cells, light emitting devices, and optical waveguide devices [4–8]. Thanks to its properties, ZnO is the most widely applied metal oxide material for monitoring various gases, especially for detecting vapours of ethanol, hydrogen, methanol, trimethylamine, ammonia, acetaldehyde, carbon dioxide, xylene, monoethanolamine, etc [9–11].

Given the high applicability of ZnO-based gas sensors in various fields such as automotive industry, monitoring of airborne pollutants, improvement of residential safety or detection of natural gas leaks, much effort is being devoted at industrial level for the development of highly sensitive nano-sensors based on ZnO [12]. In this regard, the development of gas sensors for the detection of carbon monoxide (CO) is an issue of the day, since CO is one of the most toxic gases. Because of its lack of odour, it can form undetected products by incomplete combustion of fuel in industry and in residences which convert it in one of the main environmental contaminants.

Numerous methods have been proposed for the synthesis of ZnO nanomaterials. Radio frequency (RF) magnetron sputtering, pulsed laser deposition, electrochemical deposition and chemical vapour deposition growth (CVD) are some of the most employed techniques due to various applicability of the obtained materials [1,3,4,12–14]. RF sputtering technique has been indicated as a viable method of preparing metal oxide films for CO sensing applications due to the ease in control over the preferred crystalline orientation, growth at relatively low temperature, good interfacial adhesion to the substrate, and the high packing density of the grown film [15]. On the other hand, CVD growth is used to produce high-purity bulk materials and powders, as well as fabricating composite materials via infiltration techniques [16].

As a function of synthesis method and resulting morphology, various models were proposed in order to explain the ZnO sensing properties. For example, thin films have been reported to be influenced by the crystallite size, d, of the sensor material in conjunction with the space charge depth, L, where the grain size control is recognized as the most sensitive condition [17,18]. On the other hand, in the case of nanostructured materials, other parameters such as surface-to-volume ratio and depletion layer width need to be considered in order to explain the sensing characteristics. Since the surface-to-volume ratio is strictly related to the density of the adsorbed oxygen ions, it affects at a large extent the sensor response. For example, Hongsith et al. reported a higher ethanol sensing response for both aligned high aspect-ratio nanowires and

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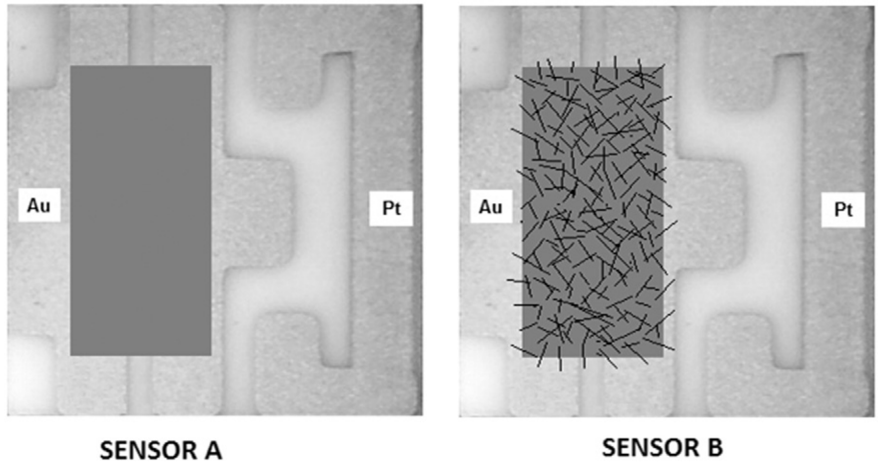

Fig. 1. Schematic of the sensor designs: sensor A = ZnO film and sensor B = ZnO film + ZnO nanowires.

spaghetti-like ones with respect to bulk or thin film [19]. Moreover, it is important to distinguish between the resistance due to potential barrier between nanowires and the resistance along the nanowire which is due to surface depletion layer and conductive channel.

Although extensive work was dedicated to ZnO gas sensors till present, no study is yet available on the surface-to-volume ratio and the depletion layer effects on sensing performance of a hybrid ZnO material. Herein, a design based on ZnO film and ZnO nanowires was employed by coupled approach using RF magnetron sputtering and vapour–liquid–solid (VLS) techniques [20,21]. The sensing properties of ZnO hybrid based on both thin film and nanowires were tested for CO gas detection in the range level of 10–50 ppm at varying operating temperature and reported to thin film ones. A comparison with the performance of films and nanowires obtained by various methods is given.

2. Experimental

2.1. Sensor design and material growth

In order to analyse the effect of surface-to-volume and depletion layer, two types of sensors were fabricated according to the design depicted in Fig. 1: while sensor A was based on solely ZnO film, sensor B was based on ZnO nanowires dispersed onto the surface of ZnO film. For this purpose, alumina plates (3×3 mm^2) previously patterned with Au contacts (50 nm thick film) and Pt heating elements (200 nm thick) were used as substrates for ZnO growth.

The ZnO film (200 nm thick) was deposited by RF sputtering technique through a shadow mask as presented elsewhere [1]. A ZnO target (two in. diameter, 99.99% purity, Lesker) was set 9 cm apart from alumina substrate and the deposition was performed at 150 W sputtering power by using high purity Ar gas as flow carrier in the chamber set at a vacuum of 2×10^{-6} Torr. On the other hand, ZnO nanowires were synthesized by a VLS process as previously reported [22].

The morphology of the obtained ZnO materials was investigated by using a FEI QUANTA 3D dual beam SEM/FIB microscope and a Dimension 3100 Atomic Force Microscope (AFM) (Digital Instruments) employed in tapping mode.

2.2. CO sensing setup

A home-made gas test set-up consisting in a thermal mass flow-controller (Bronkhorst El-Flow), instrument-grade stainless steel lines and a 150 cm^3 cell was employed. The temperature and relative humidity were continuously monitored by a temperature sensor (Pt1000) and a calibrated humidity sensor (Honeywell). The desired relative humidity and the gas concentration were generated by mixing proper flows of synthetic dry air, water vapour saturated air and certified mixtures of testing gas in air [23].

The chemo-resistive properties of the obtained sensors towards CO gas were measured by using the flow-through technique at a constant 500 cm^3 min^{-1} gas flow. Electrical resistance of the sensor was measured by using a stabilized DC source and a 6485 Picoammeter (Keithley Instruments).

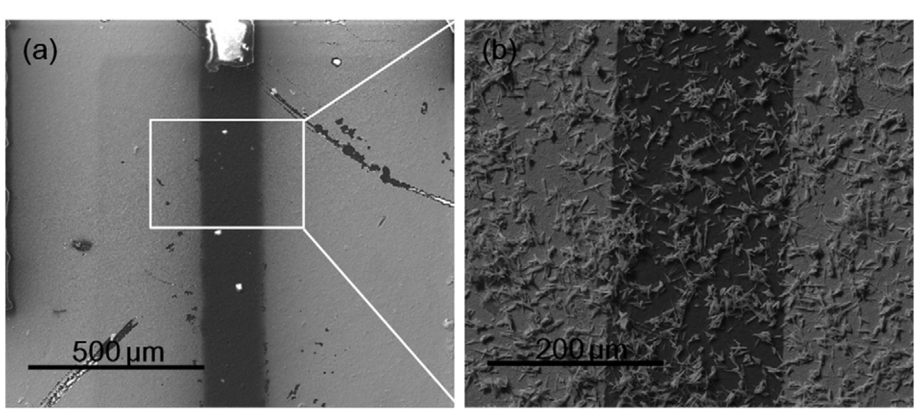

Fig. 2. SEM image of ZnO thin film based sensor (a) and SEM image of hybrid-based sensor (b).