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ZnO nano-tree active layer as heavy hydrocarbon sensor: From material synthesis to electrical and gas sensing properties

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ABSTRACT

ZnO with dense, porous, nano-wire and nano-tree morphologies was successfully synthesized via reactive magnetron sputtering at high pressure (10 Pa) and with different deposition temperatures (RT → 1273 K). The morphological properties of prepared ZnO coatings were revealed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis was performed to determine crystalline structure of the films in relation with their deposition temperature. Hall effect measurements were used to investigate the electrical resistivity, free carrier concentration and mobility in the coatings as a function of their morphology in a temperature range from 293 K to 473 K. Finally, $C_{12}H_{26}$ dodecane gas sensing properties of ZnO nano-trees were investigated at different temperatures (from 323 K to 566 K) and the results were discussed depending on dodecane concentration. A remarkable response of 39% was observed at 415 K for a low concentration of dodecane in air [1 ppm(v)]. High response to low concentrations of $C_{12}H_{26}$ as well as good chemical stability of ZnO nano-trees make this kind of structure a potential candidate as sensing layer for practical sensor applications.

1. Introduction

The problem of monitoring the lower explosive limit (LEL) of flammable gases and vapours of flammable liquids is a top priority for the gas-and-oil industry, e.g. transportation and storage of gas and oil products [1]. Jet fuel is one of the critical transportation fuels that is mainly used in commercial aircraft and military vehicles. Recently considerable interest was paid to *n*-dodecane ($C_{12}H_{26}$), as a possible alternative to petroleum-based jet fuel and other conventional aviation fuels, which represent the paraffinic and bicyclic characteristics of jet fuel and has a number of carbon atoms similar to the average molecular formula of jet fuel ($C_{11}H_{21}$) [2–4]. Aircraft accidents have a considerable impact on public opinion and *n*-dodecane is highly flammable (lower explosive limit of 0.6%) so gas leaks represent considerable explosion hazards and there is a great interest to continuous monitoring of its concentration: the leak not detected in time may cause grave damages. For monitoring of LEL flammable gases and vapours of flammable liquids, catalytic [5], semiconductor [6] and optical [7] sensors are extensively reported in the literature.

Semiconductor gas sensors present the property of changing the conductivity of the sensing material in the presence of a determinate gas. In principle, electrical conductivity of n-type semiconductor increases (or decreases) when reducing (or oxidizing) gases are adsorbed on its surface. The working temperature at which these devices are more efficient can vary depending on the gas atmosphere and on properties of the sensor material selected in every case [8].

Metal oxide semiconductor gas sensors have attracted a lot of attention due to their cheap and easy-to-use gas monitoring capabilities. It consists of three main components — sensing material, electrodes and a heater. A wide range of metal oxides such as ZnO, SnO_2, In_2O_3, MnO, WO_3, CuO, TiO_2, CeO_2, NiO, Ag and Sr doped $LaCoO_3$ with various morphologies like nanorods, nanospheres, nanoflowers, nanowires, nanoneedles, nanoflakes, nanoplatelets and nanobelts have been used to fabricate gas sensors to detect reducing and oxidizing gases at room and elevated operating temperatures [9–19]. Among these oxides which can be applied for the detection of various LEL gases, zinc oxide is an interesting II–VI compound semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV [20–22]. Due to its unique properties, ZnO has been effectively applied in various fields including piezoelectric devices [23], photocatalysis [24], antibacterial agent [25], UV-shielding materials [26], solar cells [27] and gas sensors [28]. ZnO as a gas sensor active layer has different characteristics like high chemical stability, amenability to doping, non-toxicity, low cost and chemical sensitivity to numerous gas species including acetylene (C_2H_2) [29], hydrogen sulfide (H_2S) [30], hydrogen peroxide (H_2O_2) [31], ethanol (C_2H_5OH) [32], ammonia (NH_3) [10], carbon monoxide (CO) [33] and ozone (O_3) [34]. ZnO has attracted the interest of

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Table 1
Sputtering parameters maintained during deposition of ZnO coatings.

Ar flow rate [sccm]	220	Target	Zn
O_2 flow rate [sccm]	10	Discharge current [A]	0.5
Run duration [h]	2	Pulse frequency [kHz]	50
Draw distance [mm]	100	T_{off} [μs]	5
Total pressure [Pa]	10	Substrate temperature	RT, 1023 K, 1173 K, 1273 K

many scientists due to its easy fabrication as thin film with various methods such as DC/RF sputtering, thermal evaporation, spray pyrolysis, sol–gel, solution growth, and hydrothermal. Among them, sputtering technique possesses many advantages like environmentally safe, feasibility of deposition with well-controlled composition (especially in the case of amount of doping element), good crystalline quality and possibility of morphological tailoring.

In this paper, we investigated for the first time dodecane ($C_{12}H_{26}$) sensing properties of conductive ZnO coatings deposited by DC reactive magnetron sputtering. In the first part, a particular emphasis was put on the role of deposition conditions to synthesize ZnO coatings with different morphologies (dense, porous, nano-wires and nano-trees). Carrier concentration and mobility are taken into account to understand the change of electrical conductivity with the coating morphologies. Finally $C_{12}H_{26}$ gas sensing properties of the ZnO nano-trees were measured at different temperatures (from 323 K to 566 K) and depending on dodecane concentrations in air.

2. Experimental details

2.1. Synthesis of ZnO coatings

ZnO coatings were deposited by reactive DC magnetron sputtering using metallic Zn target on a rotating substrate holder in the presence of argon–oxygen reactive gas mixtures. Dense alumina pellets (Keral 99, $\Phi = 16$ mm, thickness $= 0.63$ mm) produced by Kerafol Gmbh and MSP769 platforms (fabricated by Heraeus sensor technology) were used as substrates. The experimental device was a 90 L sputtering chamber (Alcatel 604) pumped down via a turbo-molecular pump, allowing a base vacuum of about 10^{-4} Pa [35]. The argon and oxygen flow rates introduced in the deposition chamber were controlled with Brooks flowmeters and the total pressure was measured using a MKS Baratron Gauge. The films were deposited at total pressure of about 10 Pa. The substrate holder was equipped with an electrical resistance heater placed behind the substrate-holder. The coatings were deposited at different substrate temperatures (room temperature (RT) → 1273 K) and the substrates were rotated regularly during the deposition stage (60 RPM). The Zn target (50 mm in diameter and 3 mm thick) was mounted on balanced magnetron cathode with a target-to-substrate working distance of 100 mm. The Zn target was powered by pulsed DC supply (Advanced Energy Pinnacle$^+$) with a discharge current of 0.5 A. The main sputtering parameters are summarized in Table 1.

Structural characterization of the coatings was performed by Bragg Brentano configuration X-ray diffraction (XRD) using a BRUKER D8 focus diffractometer ($Co_{K\alpha 1\ +\ \alpha 2}$ radiations $\lambda = 0.178897$ nm) equipped with the LynxEye linear detector. Diffractograms were collected under air flow during 10 min in the 20–80° angle range at a scan rate (2θ) of 0.1° s^{-1}. The morphology of the coatings on brittle fracture cross sections and on their top surface as well as film thickness were determined by a Jeol JSM 7800F field emission scanning electron microscope (SEM).

DC electrical conductivity, Hall mobility and free carrier concentration measurements were performed in the temperature range 293 K–473 K for the films deposited on dense alumina pellets by means of a homemade system based on the van der Pauw method. In order to warrant the ohmic behaviour of the four contacts, I–V curves were systematically plotted and the linear evolution was checked for all van der Pauw combinations. Measurements started at 293 K and the sample was heated up to 473 K with a ramp of 2 K·min^{-1} followed by 10 min stabilization at 473 K and a return to 293 K with the same ramp as before.

2.2. Sensor test bench

The sensor properties were investigated using a test bench that was especially built for the MSP769 modules (Fig. 1). In order to work at different temperatures MSP769 modules have an integrated heating system. The control of temperature is generated by joule effect with a resistive circuit of platinum and the temperature of MSP769 module can be increased up to 1073 K during sensor testing. The electric power applied to the heating of MSP769 is carried out using a DC power supply of 1200 W (50 A — 60 V maximum) manufactured by TTi (reference QPX1200). The temperature of the MSP769 module is controlled by means of the Pt1000 Class B lower layer of the module and the resistance measurements were performed using a frame grabber of National Instrument USB-4065. A dilution bench is used in order to expose the ZnO nano-trees to synthetic air or dodecane balanced in synthetic air (pollutant gas). The sensor was exposed to a constant gas flow rate of about 200 mL·min^{-1}. In this study, before the test of sensor, an education process for stabilization of electrical conductance of the sensor is indispensable by two heating/cooling cycles (in synthetic air from RT to 723 K). After this education step, for each dodecane concentration in air [from 0 to 300 ppm(v)], the sensor's electrical response was evaluated by recording the variation

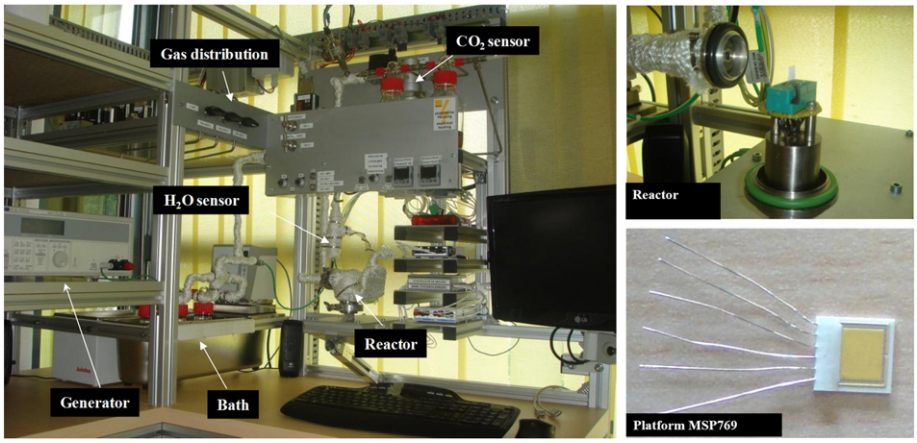

Fig. 1. Sensor test bench and MSP769 module (fabricated by Heraeus sensor technology).