Sensors and Actuators B 251 (2017) 781–794

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Self-heating effects on the toluene sensing of Pt-functionalized SnO_2–ZnO core–shell nanowires

Jae-Hun Kim [a], Hyoun Woo Kim [b,*], Sang Sub Kim [a,*]

[a] Department of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea
[b] Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea

ARTICLE INFO

Article history:
Received 2 December 2016
Received in revised form 31 March 2017
Accepted 18 May 2017
Available online 25 May 2017

Keywords:
Self-heating
SnO_2–ZnO core–shell
Pt
Toluene
Nanowires

ABSTRACT

Embedding chemical sensors into mobile devices is an emerging demand in modern information converged technology. The unbearable power consumption to raise the temperature of chemoresitive-type chemical sensors makes it impossible for them to be embedded regardless of their peculiar sensing properties such as low cost, miniaturization, high response, and excellent stability and robustness. In this study, self-heated nanowire sensors were prepared by exploiting the synergic effect of the core–shell structure and catalytic nanoparticles. As a prototype approach, Pt nanoparticle-functionalized SnO_2–ZnO core–shell nanowires were synthesized, demonstrating extremely striking performance and characteristics. Thicker ZnO shell showed the larger self-heating and higher sensor response. The sensors exhibited excellent selectivity for toluene gas, with negligible responses to other reducing gases. This one possessed a considerable sensing performance at room temperature, even without a significant self-heating. The self-heated sensing of the novel core–shell nanowires developed required only an extremely low power consumption of 31 μW, suggesting their potential in applications as sensors embedded into mobile devices.

1. Introduction

In modern industrialized society, smart sensors that can provide real-time information about gaseous chemical analytes are essential in a variety of areas. Potential applications include artificial olfaction, disease diagnosis, environmental emission monitoring, and terror defense. Chemoresistive-type metal oxide semiconductor chemical sensors are superior to other types of chemical sensors, such as electrochemical, optical, and acoustic-based chemical sensors; these include their low-cost preparation, small size and ease of miniaturization, flexibility in mass production, and simple operation [1–4]. Accordingly, metal oxide semiconductor gas sensors have been intensively studied [3,5–9]. However, there is one critical drawback of semiconductor chemical sensors: their operating temperatures are typically between 100 and 400 °C. These high temperatures are needed to ensure high sensitivity, as well as response and recovery times short enough to be applied in actual sensor devices, because these times are largely dependent on the nature of interactions and their kinetics during adsorption/desorption of analyte molecules onto/from surfaces of semiconducting sensor materials [10,11]. This means that a certain amount of external heating is inevitably needed for the activation of chemoresistive-type semiconductor chemical sensors. In general, a sensor device will include an integrated heating element having power consumption as great as hundreds of milliwatts. The use of a carefully designed, cavity-type micromachined Si platform for coupling a microheating element and a micro-sized sensor device is a strategy that can cut the power consumption down to tens of milliwatts [12]. Also, the application of an electrothermal mechanism in carbon nanotube (CNT) sensors can reduce power consumption [13]. Despite such improvements, the power consumption of external heat sources can still be a big burden in battery-powered portable devices such as mobile phones and tablets.

Self-heating of the sensor material is a promising strategy to reduce energy consumption. Salehi et al. were first to report on this strategy; they applied an AC bias to self-heat a SnO_2 carbon monoxide sensor and demonstrated its operation without an external heat source [14]. Strelcov et al. reported evidence that applying a higher bias voltage increased the gas sensitivity of metal oxide nanowires by providing more Joule heating and thus enhancing the surface sensing reaction [15]. Furthermore, Lu et al. carried

* Corresponding authors.
E-mail addresses: hyounwoo@hanyang.ac.kr (H.W. Kim), sangsub@inha.ac.kr (S.S. Kim).

http://dx.doi.org/10.1016/j.snb.2017.05.108
0925-4005/

out room-temperature methane sensing using suspended CNTs, experimentally demonstrating that the power consumption can be reduced by decreasing the sample size [16]. Fan et al. showed that self-heating was more effective in one-dimensional nanolines than in two-dimensional films [17], and Strelcov et al. suggested that power consumption in nanowire (NW) sensors was reduced not only by decreasing the NW diameter but also by increasing the NW length [18].

Although power on the order of a few hundred milliwatts is required to heat the sensors by means of microheaters [11], the sensor power consumption can be reduced to a few milliwatts by using palladium (Pd) NWs [19], Pd-loaded single-walled CNTs [15], or Pt-coated $W_{18}O_{49}$ NW networks [20]. Furthermore, ultralow power consumption on the order of a few tens of microwatts has been achieved: for example, sensors based on individual NWs have exhibited the power consumption of 27 μW [21], a sensor based on WO_3 thin film nanostructures consumes only 21.6 μW [22], and suspended CNT sensors have been operated at the unprecedentedly low power of 2.9 μW [23].

However, the low-power sensors just mentioned are typically not easy to integrate into high-yield and low-cost mass production processes, and selective detection has not yet been achieved with self-heated nanomaterials. Moreover, the applied voltage needed to induce self-heating has often been over 10 V, which is another barrier for actual application. Note that the applied voltage is not for an external heating source, but for the measurement of sensor resistance. These obstacles need to be surmounted before chemoresistive-type chemical sensors can be embedded into hand-held portable devices. In our recent results [24], the utilization of the core–shell (C-S) structure was particularly effective in detecting reducing gases. The amount of electron depletion in the shell layer will be varied, becoming the dominant mechanism whereby sensing of reducing gases by C-S NWs can be improved.

In addition, the addition of metal nanoparticles (NPs) onto the surface of the shell layer functionalizes the C-S nanostructures, further enhancing their sensing capabilities. Noble metal NPs can be a catalyst for a particular gas, and even further improves the sensing abilities [25]. Noble metal NPs will provide a spillover effect, facilitating the adsorption, dissociation, and transfer (to the adjacent nanowire surface) of target gases. Also, the metal/shell heterointerface will generate an energy barrier, contributing to the modulation of resistance and thereby increasing the sensor response.

Toluene (C_7H_8) is a volatile organic compound (VOC), which is extensively used in the production of paints, lacquers, adhesives, rubbers and many other industrial products. However, it is a toxic compound and can affect the central nervous system, liver, kidneys, and skin [26,27]. Also, sick building syndrome, which refers to health issues building occupants experience, such as headaches, nausea, eye irritation and cough, is caused by VOCs, including C_7H_8 [28]. Furthermore, C_7H_8 is a biomarker of lung cancer [29]. Therefore, there is an urgent need to detect C_7H_8 accurately and reliably. The key purpose of the present work was to realize highly sensitive/selective detection of C_7H_8 gas with ultralow power consumption by means of self-heating in a hybrid structure comprised of core–shell NWs and metal functionalization without an external heating source. We expected that the C-S NW structure would promote self-heating effects. The use of core–shell NWs provides improved detection capability for reducing gases, and the metal functionalization adds catalytic sensitization for a specific gas. As a result of the synergic effect of these two components, the present hybrid sensor exhibited selective detection of C_7H_8 under an applied voltage as low as a few volts for the measurement of sensor resistance, showing its promise for embedment into a portable device.

2. Experimental

2.1. Preparation of networked SnO_2–ZnO C-S NWs

SnO_2–ZnO C-S NWs were synthesized by means of the following two steps. First, highly networked SnO_2 NWs were grown by means of a vapor–liquid–solid method, including the evaporation of a Sn source. The experimental procedure for this fabrication has been described previously [30] and is summarized briefly as follows. A patterned interdigital electrode (IDE) consisting of Au (3 nm thick), Pt (200 nm thick), and Ti (50 nm thick) layers was fabricated by means of a conventional photolithographic process on a SiO_2 (200 nm thick)/Si (100) substrate. SnO_2 NWs were selectively grown on the IDE in a horizontal tube furnace at 900 °C for 15 min under N_2 and O_2 gases, producing networked junctions by means of the entanglement of neighboring SnO_2 NWs over the areas between the electrode's digits.

Following this, we coated the networked SnO_2 NWs with ZnO shells by means of an atomic layer deposition (ALD) technique [31]. Diethylzinc ($Zn(C_2H_5)_2$) and H_2O were used as the precursors, and the temperature and pressure were respectively set at 150 °C and 0.3 Torr. Each cycle of the ALD process comprised of diethylzinc dosing for 0.12 s, N_2 purging for 3 s, H_2O dosing for 0.15 s, and N_2 purging for 3 s. The thickness of the ZnO shells was controlled by varying the number of ALD cycles; the shell thickness increased linearly with increasing number of ALD cycles. This relationship was described in detail in a previous report [27]. For the purpose of this work, we prepared SnO_2–ZnO C-S NWs with various shell thicknesses by varying the number of ALD cycles.

2.2. Functionalization of the NWs with Pt NPs via gamma-ray radiolysis

We attached Pt NPs to the SnO_2–ZnO C-S NWs by means of a gamma-ray radiolysis technique. The experimental procedure for the gamma-ray radiolysis has been described in our previous paper [32] and is briefly summarized as follows. As a precursor solution, we used 1.0 mM hydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot nH_2O$, $n = 5.8$, Kojima Chemicals Co.), in a mixture of deionized water (94 vol.%) and 2-propanol (6 vol.%). The SnO_2–ZnO C-S NWs were immersed in the precursor solution and then exposed to ^{60}Co gamma rays in air under ambient conditions (Korea Atomic Energy Research Institute). The samples were exposed to gamma rays of the illumination intensity 10 kGy h^{-1} for 2 h.

2.3. Materials characterization

The microstructure of the synthesized samples was observed by means of field-emission scanning electron microscopy (FE-SEM). The crystal structure, microstructure, and chemical composition were examined in detail by means of X-ray diffraction (XRD), TEM, and energy-dispersive X-ray spectroscopy (EDS). The Pt NPs were synthesized and attached to the SnO_2–ZnO C-S NWs via gamma-ray radiolysis. The Pt NPs, which were approximately 20 nm in diameter, were uniformly distributed on the C-S NWs, confirming that gamma-ray radiolysis is an effective technique for creating metal NPs on metal oxide NWs.

2.4. Sensing measurements

We investigated the C_7H_8 sensing performance of the Pt NP-functionalized C-S NWs. The sensing temperature ranged from 25 to 200 °C. The concentration of target gas was controlled by means of controlling the mixing ratio of the target gas to dry air using accurate mass flow controllers (MFCs). The total flow rate was fixed at 500 sccm. According to the manufacturer's specifications, the con-