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Utilization of both-side metal decoration in close-packed SnO_2 nanodome arrays for ultrasensitive gas sensing

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ABSTRACT

Metal decoration on hollow metal oxide nanostructures is an attractive route to enhance gas sensing properties. Herein, we present a facile method for the utilization of metal decoration on both the inner and outer surfaces of hollow metal oxide nanostructure for the first time. Close-packed SnO_2 nanodome arrays decorated with Au nanoparticles are fabricated by soft-template method and self-agglomeration of an Au film. The position of Au decoration for SnO_2 nanodome arrays is controlled by changing the deposition sequence of Au and SnO_2 films. While inside, outside, and both-side Au-decorated SnO_2 nanodome arrays show much higher responses to various gases than a bare SnO_2 nanodome, it is shown that the response of both-side Au-decorated SnO_2 nanodome arrays to C_2H_5OH at 300 °C is 18 times higher than that of the bare SnO_2 nanodome arrays and the theoretical detection limit is below 1 ppb. These are attributed to the catalytic effect of Au nanoparticles on the modulation of barrier potentials in links between the individual SnO_2 nanodomes. Our results demonstrate that the utilization of both-side metal decoration is an effective strategy for enhancing the gas sensing performance of hollow metal oxide nanostructures.

1. Introduction

Gas sensors are widely used in diverse areas such as automotive, aerospace, domestic, and security industries in order to detect, monitor, and control the harmful, toxic, hazardous, and flammable gases [1–3]. In addition, their applications have been reaching emerging fields such as noninvasive diagnosis of human diseases [4–7]. Recent studies have shown that the various diseases including lung cancer, asthma, diabetes, renal diseases, and halitosis can be diagnosed by detecting gaseous biomarkers such as H_2S, NO_x, and volatile organic compounds from exhaled breath [8–10]. Various gas sensors, including optical sensors, electrochemical sensors, surface acoustic wave sensors, and semiconductor metal oxide sensors have been demonstrated for breath analyser applications [11–13]. Among them, semiconductor gas sensors based on metal oxides are very promising as sensing elements for breath analysers due to their irreplaceable advantages such as cost-effectiveness, simplicity in fabrication, small size, and easy integration with electronic circuits [14,15]. For a semiconductor gas sensor, the gas sensing performance is significantly improved by increasing the surface-to-volume ratio of the sensing film [16]. Accordingly, over the past decade, low dimensional nanomaterials with large specific surface area have been predominantly investigated. Despite the efforts, how to integrate them with low-cost and high-yield mass production process still remains challenging. Also reliable and reproducible gas sensing properties are often hard to be obtained due to nonuniform connections between randomly distributed individual nanomaterials [17,18].

An alternative route to achieve highly sensitive and reliable semiconductor metal oxide gas sensor is the use of soft-templating

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which is facile way to make various nanostructure depending on the shape of the sacrificial template [19,20]. Polystyrene or poly(methylmethacrylate) nanobeads are commonly used for sacrificial templates because they can be formed in close-packed arrays and easily removed by annealing at high temperatures, leading to highly ordered dome-like hollow structures [21]. These attractive advantages have already been identified them as the applications for high response metal oxide gas sensors [22]. Especially, the recent report by Dai et al. showed the utilization of monolayer polystyrene nanobeads templates on 4 inch Si wafer for highly sensitive gas sensors based on hollow metal oxide nanostructures [23].

Gas sensing properties of hollow metal oxide nanostructures can be enhanced by metal decoration on the surface because metal nanoparticles on the surface play as chemical and electronic sensitizers [24,25]. Generally, metal decoration on the surface of porous metal oxide nanostructures is performed using physical vapor deposition (PVD) of metal films and subsequent self-agglomeration into nanoparticles during the deposition or post-annealing, which leads to the relatively uniform coverage of metal nanoparticles on the surface and thermal stability for long-term operation compared to a drop coating method [26]. However, metal nanoparticles are formed only on the outer (top) surface of metal oxide nanostructures [24]. Consequently, both the outer and inner surface could not be utilized for metal decoration to further enhance the gas sensing properties. Therefore, a new method is necessary for enabling both the outer and inner surface of hollow metal oxide nanostructures to be functionalized by metal nanoparticles.

In this paper, in order to overcome the aforementioned limitation, we present a facile and effective strategy for the utilization of metal decoration on both the inner and outer surface of hollow metal oxide nanostructures using PVD for the first time. Highly ordered SnO_2 nanodome arrays with both-side Au decoration have been achieved using soft templates of polystyrene nanobeads. The deposition of an Au film is controlled to make the outer and/or inner surface of close-packed SnO_2 nanodome arrays decorated with Au nanoparticles and responses to various gases such as C_2H_5OH, H_2, CO, CH_4, C_7H_8, and CH_3COCH_3 have been measured at 300 °C. Our results show that the gas response of both-side Au-decorated SnO_2 nanodome arrays to ethanol is 18 times higher than that of bare SnO_2 nanodome arrays and the theoretical detection limit is below 1 ppb, which are mainly attributed to the formation of large-barrier double Schottky junctions between individual nanodomes.

2. Experimental

2.1. Fabrication

180-nm-thick Pt films were prepared on SiO_2/Si substrate using an electron beam evaporator at base pressure of 2×10^{-6} mTorr. Before Pt deposition, 20-nm-thick Ti was deposited for the good adhesion of Pt to the substrate. For gas sensor application, interdigitated electrode (IDE) patterns of 5 μm spacing were fabricated on the Pt/Ti films using photolithography and dry etching. The Pt-IDE-patterned SiO_2/Si substrate was treated by O_2 plasma using a microwave plasma etcher (Plasma Finish V15-G) at a working pressure of 400 mTorr (O_2) and an rf power of 150 W for 3 min to make the surface hydrophilic. An aqueous suspension of 700-μm-diameter polystyrene beads (2.6 wt%, Polysciences, Warrington, U.S.) was used to prepare a close-packed monolayer nanobead template on the Pt-IDE-patterned SiO_2/Si substrate via spin coating at a speed of 1000 rpm for 2 s. After the spin coating, the sample was dried for 1 h in a dry box at room temperature to evaporate the solution. Approximately a 2-nm-thick Au film was firstly deposited onto the monolayer nanobead template by an electron beam evaporator and then a 100-nm-thick SnO_2 film was deposited by a RF sputter using a polycrystalline SnO_2 target on the Au film deposited polystyrene monolayer template. The base pressure, working pressure, rf power, gas flow rate and growth rate were 2×10^{-6} mTorr, 10 mTorr, 100 W, 30 sccm (Ar) and 10 nm/min, respectively. A 2-nm-thick Au film was again deposited on the SnO_2-coated template. Finally, the sample was calcined in air at 550 °C for 1 h to burn out the polystyrene nanobeads and crystallize the SnO_2 film, which leads to the formation of SnO_2 nanodome arrays and simultaneously to the agglomeration of Au films to Au nanoparticles on both the inner and outer surface of SnO_2 nanodomes.

2.2. Characterization

The morphology of the fabricated SnO_2 nanodome arrays was characterized by an environmental scanning electron microscope (XL30 FEG ESEM, FEI) using an acceleration voltage of 15 kV and a working distance of 10 mm. Transmission electron microscopy (TEM) was performed using a JEM-2100F field emission transmission electron microscope (JEOL, Peabody, U.S.). For the TEM analysis, the specimen was prepared by mechanical polishing followed by ion milling with Ar ions (FIB, FEI-Helios).

2.3. Sensor measurements

Gas sensing properties of the Au-decorated SnO_2 nanodome arrays were measured in a quartz tube with external heating. The flow gas was changed from dry air to a calibrated target gas (balanced with dry air, Sinyang Gases). A constant flow rate of 500 sccm was used for the dry air and target gas. The response of the Au-decorated SnO_2 nanodome arrays was accurately determined by measuring the baseline resistance in dry air and the fully saturated resistance after exposure to the target gas. The resistances were measured at a DC bias voltage of 1 V using a source measurement unit (Keithley 236). The gas flow was controlled using mass flow controllers and all measurements were recorded on a computer using LabVIEW over the GPIB interface. Additional experimental details about sensor measurements may be found in our previous reports [24].

2.4. Calculation of theoretical detection limit

The detection limit could be derived from the sensor's signal processing performance. We took 10 resistance points at the baseline prior to an exposure to C_2H_5OH. And then a fifth-order polynomial fit was implemented within the data-point range, which gives both the curve-fitting equation and the statistical parameters of the polynomial fit.

$$Vx^2 = \sum (y_i - y)^2$$

where y_i is the measured data-point and y is the corresponding value calculated from the curve-fitting equation. The rms noise was calculated as

$$\mathrm{rms}_{\mathrm{noise}} = \sqrt{\frac{Vx^2}{N}}$$

where N is the number of data points used in the curve fitting. The theoretical detection limit (DL) could be calculated using the following equation.

$$\mathrm{DL(ppm)} = 3\left(\frac{\mathrm{rms}}{\mathrm{slope}}\right)$$

More details about calculation of theoretical detection limit may be found in previous report [27].