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ZnO-nanowire size effect induced ultra-high sensing response to *ppb*-level H_2S

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ABSTRACT

Presented is nano-size effect of ZnO nanowires (NWs) on sensitivity of hydrogen sulfide (H_2S) detection in ambient atmosphere. The sensing mechanism of ZnO NWs for H_2S detection is found coming from nano-size effect that governs both the sulfuration reaction when H_2S is introduced and the following desulfuration reaction when the gas is removed from air. Based on the nano-material property of smaller dimension featuring higher chemical-activity at surface, the sensitivity of ZnO NWs to ultra-low concentration H_2S is expected to be increased by shrinking the NW diameter. In our experiment, suspended micro hotplates for chemiresistive sensing are fabricated to investigate the nano-size sensing effect. Besides conventional ZnO NWs with the diameter as 50 nm, a novel tree-branched nano-structure of ZnO NWs (with the branch diameter as 20 nm) is *in situ* grown onto the sensing-area of the micro hotplate. In order to investigate the sensing effect, both the 20 nm NW sensor and the 50 nm NW sensor are used to experimentally detect H_2S with concentrations in the range of *ppb-ppm*. The 20 nm ZnO-NWs sensor realizes resoluble sensing to 5 ppb H_2S, while the 50 nm sensor can only response to H_2S with concentration higher than 50 ppb. The well validated nano-size effect of thinner NWs featuring higher sensing response can be extended for various chemical sensing nano-materials.

1. Introduction

Hydrogen sulfide (H_2S) is a kind of toxic, corrosive and inflammable gas. Gaseous H_2S has distinct fetor of rotten egg that is commonly formed in nature and released during the decay of organic matter. The H_2S gas is normally generated from sewage, coal mines, and petroleum/natural gas industries, and it is widely utilized in various chemical industries. When the gas concentration of H_2S is higher than 250 ppm, it may lead to death [1]. Even at lower concentration level, H_2S is harmful to human bodies. The harmful H_2S molecules can be rapidly absorbed by human's lung and easily cause respiratory system disease, unconsciousness neurological sequelae and cardiovascular-related death [2]. Recently recognized as an important endogenous gas, H_2S can be implicated in diverse physiological and pathophysiological process, such as regulation of inflammation, brain development, blood pressure regulation and metabolism [3–9]. It has been reported that the hydrogen sulfide in human body is at *ppm* or sub-*ppm* level, and it is indicated that trace-concentration detection of H_2S is helpful for disease diagnosis [10]. For accurate analysis and early-stage prognosis of diseases, H_2S detection at sub-*ppm* or lower concentration is highly demanded. Numerous chemical sensors have been investigated and developed, which are mainly based on metal-oxide semiconductor sensing [11,12], electrochemical detection [13] and optical measurement [14]. However, the lack of effective detection method and analytical tools for monitoring of trace-concentration H_2S has hindered the biomedical research that is correlative with the endogenous gas [15]. Therefore, it is of great importance to develop *ppb-ppm* level detectable H_2S sensors.

Several technical approaches have been reported to improve sensing performance of H_2S sensors. At present, the H_2S sensors by using semiconducting metal-oxide nano-materials are attractive due to high sensitivity. For example, ZnO, In_2O_3 and SnO_2 [16–20] can specifically response to the presence of the gas by changing electronic conductivity, thereby having been widely used in various applications like industrial safety, product quality control, clinical diagnostics and home-safety alarms. Among the various investigated metal-oxide sensing materials, n-type ZnO nanowires (NWs) materials have been intensively explored and

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widely used for gas sensing, due to their high mobility of conductive electrons, good chemical/thermal stability and low cost [21–24].

In recent years, ZnO nanostructures have been used for building chemiresistive H_2S sensors [25] and the measure range of these H_2S sensing devices generally focus in *ppm* level [26]. Thanks to the high surface-to-volume ratio, the nano-structured materials provide large adsorbing interface that indeed helps to increase sensitivity [27]. For instance, mesoporous thin-films or nanowire arrays have shown several folds enhanced H_2S sensing properties compared to the traditional sensors that are based on solid-state thin-film sensing materials [11,28]. However, to the best of our knowledge, it is really difficult to improve sensitivity by tens of folds or more by only using the increasing surface-to-volume method. Being an exception, our group recently reported that, when the diameter of ZnO wires is reduced to tens of nanometers, a sulfuration-desulfuration dual-stage sensing mechanism becomes to dominate and induces dramatically enhanced sensitivity. 50nm-diameter ZnO NWs can detect 50 ppb H_2S due to the dual-step reaction [29]. This new sensing mechanism can be originated from nano-size effect. When ZnO NWs are thin enough, the surface becomes active enough to be sulfurated by H_2S to form ZnS. This decreases the number of adsorbed oxygen molecule from ambience and causes thinner electron depletion layer. The sulfuration leads to drastic decrease of the ZnO resistance and enhance the sensing signal. After H_2S is removed, the metastable intermediate of ZnS will be quickly desulfurized back to ZnO by the ambient oxygen and the resistance quickly recovers to its initial state. This two-step reaction sensing mechanism is different from the widely used conventional one for detecting reductive gases in ambient air. The mechanism for conventional metal-oxide sensors is based on semiconductor resistance change which comes from electron depletion layer variation induced by surface adsorbed oxygen species [30]. When H_2S molecules react with the oxygen species, the change of depletion layer causes variation of ZnO resistance and outputs the sensing signal [17,31]. It has been reported that bulk-material of ZnO responds to H_2S with the concentration at tens of *ppm* level [11] while the 50 nm ZnO NWs sensor features reversible sulfuration-desulfuration sensing mechanism and outputs response to 50 ppb H_2S. Obviously, nano-size effect brings the high sensing performance. Along with size shrinkage of the nano-material, the confinement of bulk to surface becomes weaker and the material surface becomes more active. Compared with the sensitivity improvement caused by the increased surface-to-volume ratio, the nano-material size effect induced improvement in sensitivity is much more significant [29].

This work is just inspired by the sulfuration-desulfuration H_2S sensing mechanism for ZnO of nano-diameter. Herein, it is expected that continuously thinning the ZnO NWs induces continuously enhanced active surface and improved sensitivity. Therefore, herein we conceive to explore the ZnO nano-size effect on H_2S detection performance. For the purpose, the method for *in situ* grown thinner ZnO NWs than 50 nm is studied. Finally, we develop a technique to region-selectively grown tree-branched 20 nm ZnO NWs at the comb-shaped electrode region of a chemiresistive sensing micro-chip. The sensing microchip consists of a suspended micro-hotplate where the pair of comb electrodes is accommodated for the sensing nano-material growth. Finite element modeling (FEM) thermal simulation is performed to optimize the sensor structure and improve temperature uniformity across the micro-hotplate. For H_2S sensing experiment, 20 nm ZnO NWs and the conventional 50–60 nm ZnO NWs are grown, respectively. The detectable results of 5 ppb H_2S by using the 20 nm ZnO NWs well proves the regulation effect of ZnO nano-size on H_2S sensitivity.

2. Experimental

2.1. Design and fabrication of suspended sensing micro-hotplate

Micromachined hotplates for gas sensors are advantageous in thermal isolation, low power consumption and low-cost manufacturing [32–34]. In this work, a sandwich-structured micro-hotplate comprises comb-finger electrode layer, intermediate SiO_2 isolating layer and heating resistor layer. The three-layer structure is formed on a suspended silicon nitride beam-plate. Fig. 1 shows our designed micro-hotplate for gas sensor. The suspended plate is connected with four narrow supporting beams that are clamped to silicon substrate and the geometry is optimized to minimize thermal conduction to outside. The circular plate is 300 μm in diameter and each support beam is 150 μm in length and 20 μm in width. The radial platinum resistor is for heating the plate, as platinum features very linear temperature coefficient of resistance (TCR) for easy temperature calibration. The resistance versus plate temperature is pre-calibrated in a precise oven. Above the Pt heater, a thin layer of SiO_2 is employed to insulate the heater and the electrodes at top. To measure the chemiresistance change of ZnO NWs, a pair of comb-finger electrodes is densely placed above. The gap distance between the two comb-fingers is 10 μm, which can be electrically bridged by the grown branching ZnO NWs into a chemiresistor. As is shown in Fig. 1(b), the ZnO NWs will *in situ* grown at the central sensing area, i.e., over the comb-finger electrodes. The sensor has four interconnection lines, with two for the micro-heater and the other two for chemiresistance signal readout.

By using silicon micromachining technology, the chip is fabricated in single-side polished (100) silicon wafer, with the process steps sketched in Fig. 2 and described as follows: (1) Deposition 1 μm-thick low-stress silicon nitride by low pressure chemical vapor deposition (LPCVD). (2) A 30 nm/300 nm Ti/Pt composite thin-film is deposited by electron-beam evaporation and patterned by lift-off process to form the heater. (3) A 400nm-thick insulating layer of SiO_2 is formed using plasma enhanced (PE) CVD. The contact holes for the Pt heater are opened. Then, a 30 nm/300 nm-thick Cr/Au layer is evaporated and patterned to form the comb-finger electrodes and the wire-bonding pads of the Pt heater. (4) The SiO_2 and silicon nitride layers are sequentially etched by reactive ion etching to form the shape of the suspended plate and the beams. (5) The silicon beneath the plate is etched off by isotropic etching of vapor-phase XeF_2 and the micro plate is released for free-standing. After the wafer is diced, the chips are mounted on PCB and wire bonding is implemented. At this step, the chip is ready for *in situ* growth of ZnO NWs sensing material. It is worth pointing out that the metal materials used in the micro sensor can sustain the temperature process during synthesize of ZnO NWs.

2.2. In situ grown of ZnO NWs

The ZnO NWs, with the diameter as about 50–70 nm, are synthesized from aqueous solution and *in situ* grown at the sensing area of the sensor by using a modified hydrothermal method [35] and shown in Fig. 3(1)–(2). The surface of the sensor is plasma pretreated (with Harrick PDC-002 equipment) for 5 min to eliminate surface contamination. Afterwards, 5 mM zinc acetate in ethanol is dropwise coated in the sensing area by using a commercial micromanipulator (Eppendorf, PatchMan NP2), with the aid of inspection under a microscope (Leica, DM4000). Later, the sensor chip is dried in air for 10 s, rinsed with ethanol and then, blow dried with a pure nitrogen stream. This coating step needs to be repeated for at least three times. Covered with the seed film of zinc acetate crystallites, the seeded chip is heated to 350 °C in air for 20 min to yield a nanolayer of ZnO seeds. Then, ZnO NWs are *in-situ* grown at the surface of the chip by using hydrothermal method with an aqueous solu-