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WO_3 nano-rods sensitized with noble metal nano-particles for H_2S sensing in the ppb range

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ABSTRACT

Hydrothermally grown hexagonal WO_3 nano-rods were sensitized by additional Pt and Au nano-particles. The size of the 20–29 nm noble metal nano-particles were stabilized with methoxy-polyethylene glycol, and their solution was mixed with the tungsten-oxide nano-rod suspension. Controlled sized suspension drops of activated and pure reference material were deposited on the top of micro-hotplate with gold interdigital electrodes on top. The gas sensitive properties were measured for NH_3 and H_2S in a temperature range of 140–300 °C. Noble metal nano-particles multiplied the gas sensitivity for H_2S, whereas no significant effect could be detected for NH_3. With gold nano-particles a lower detection limit of 25 ppb could be achieved. The response time is in the range of 30–80 s, whereas typically 300 s is needed for complete recovery.

1. Introduction

The improved performance of conductivity type nano-structured metal-oxide gas sensors gave a new impulse to the development of novel materials, processing techniques and devices. As the Debye length is comparable with the characteristic crystal size, the increased sensitivity of the nano-sized structures enables the detection of hazardous gases even in the ppb range [1–4]. The most intensively investigated transition metal-oxides are SnO_2 [5–7], ZnO [8,9], MoO_3 [10,11], WO_3 [12–15], Fe_2O_3 [16,17]. Sensing layers formed from these oxides can be characterised by their crystal shapes and geometry, such as nano-powders, nano-spheres [4,18], nano-wires [19,20], nano-belts [19,21] and nano-rods [8,22]. The building blocks of nano-powders and nano-spheres are 0D crystals of less than 30 nm size, whereas nano-wires and nano-belts can be treated as quasi 1D structures featured by diameter of 10–30 nm and several micrometer in lengths [23]. The 100–500 nm diameter nano-rod structures can be built up from bundles of nano-wires or grown as single crystal. Typical examples of these two forms are the hydrothermally synthesised WO_3 [24] and ZnO [25], respectively.

Another issue is the elaboration of the various processing techniques to form gas sensitive layers. Beside conventional PVD and CVD techniques [13,18,26], novel processes have been introduced to build up these layers from nano-particles. Sensors reported are formed by pulsed laser deposition (PLD) [27], solvothermal process by using sacrificial carbon nano-spheres or surfactant molecules [18], nano-patterning with Langmuir-Blodgett technique [28], electrospinning [29] and a large variety of hydrothermal methods [4,22,24]. Additional techniques are also introduced to enhance sensitivity and selectivity by doping the nano-structured layers with noble metals [5,6,30–33].

Although the phenomenon is well-known and attractive results have been reported at demonstration level, most of these sensors still need to be further developed to exhibit appropriate parameters required by commercialized devices. Present work describes a step towards development of hexagonal WO_3 nano-rod based system aiming at enhanced sensitivity and selectivity with controlled characteristic size and doping techniques. In our previous work [24,34] we presented the properties and performance of hydrothermally grown hex-WO_3 nano-rods. Here we demonstrate the selective sensing of H_2S in the sub ppm range by doping the nano-rods with noble-metal particles.

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2. Experimental

2.1. WO_3 nano-rods

Uniform, hexagonal WO_3 nano-rods of 80–150 nm diameter and 4–5 μm length were synthesised by hydrothermal method according to Ref. [24].

WO_3 sol was prepared by dissolving sodium tungstate in distilled water, followed by acidification by HCl solution. The precipitate was generated by oxalic acid and the obtained WO_3 solution was transferred to an autoclave, and then Na_2SO_4 was added to the sol and maintained sealed at 180 °C for 24 h in order to prepare the hexagonal structure. The precipitates were filtered, washed with water and ethanol carefully to remove possibly remaining ions from the final products.

2.2. Gold nano-particles (~29 nm)

Gold nano-particles were synthesised by the traditional Turkevich method [35]. A solution made from 222 ml distilled water and 6 ml 0.01 M $HAuCl_4$ trihydrate was heated to boil. 6 ml sodium citrate solution (containing 0.0684 g sodium citrate trihydrate) was added into the boiling solution and boiled for 15 min before cooling it down to room temperature. These nano-particles were used as seeds to grow the larger (~29 nm) particles. 4 ml of a 0.2% (w/w) $HAuCl_4$ solution was diluted to 20 ml. After that 0.5 ml of a 1% (w/w) citrate solution was added to 1 ml of a 1% (w/w) ascorbic acid solution, and the whole solution was diluted to 20 ml. In the next step 6 ml seed solution was diluted to 20 ml and boiled, then the above described two solutions were added. The nano-particles in large excess were PEGylated using thiol functionalized mPEG-SH (methoxy-polyethylene glycol) with 2000 Da average molecular weight. 1.1498 g of mPEG-SH was dissolved in 1 ml of distilled water in ultrasonic bath by avoiding heating of the sample. This solution was added quickly to 20 ml of a citrate stabilized gold nano-particle solution and stirred for 3 h. The PEGylated nano-particles were cleaned by centrifuging and re-dispersing in water [36].

2.3. Platinum nano-particles (~20 nm)

3.6 ml of a 0.2 M solution of chloroplatinic acid hexahydrate was added to 46.4 ml of boiling distilled water. After 1 min, 1.1 ml of 1 M sodium citrate solution was added followed by a quick injection of 0.55 ml of the freshly prepared sodium borohydrate (0.08 M) solution containing 1 M sodium citrate. After 10 min the product was cooled down to room temperature. These nano-particles were used as seeds to grow the larger (~20 nm) particles. 1 ml of the platinum seed solution was diluted by 29 ml DI water at room temperature. A 0.045 ml of a 0.4 M chloroplatinic acid hexahydrate was added, followed by mixing with 0.5 ml solution of 1 M sodium citrate and 1.25 M L-ascorbic acid. Under stirring, the temperature was slowly increased to the boiling point (~10 °C/min). The reaction time was 30 min [37].

2.4. Sensor chip

Full membrane type micro-hotplate chip containing gold interdigital electrodes on top were used for all experiments. The characteristic 0.057 mW/°C specific heat dissipation allows low power operation up to 600 °C. Details of chip processing are described elsewhere [38]. In present work the operation temperature was maximized at 300 °C to avoid hexagonal/monoclinic phase transition of the WO_3 nano-rods.

2.5. WO_3 nano-rod layers sensitized with gold and platinum nano-particles

WO_3 powders prepared above were dissolved in ethylene-glycol-water-ethanol solution (0.05 mM) and mixed with solution containing 1 nM stabilized nano-particles (Au, Pt). The mixture was agitated by ultrasonic treatment for 5 min, and then a single drop was transferred onto the surface of each micro-hotplate. The applied micro-capillary transfer method forms ca. 200 μm diameter spot of the sensing layer. After a ramp up heating of 15 °C/min the chip was annealed at 200 °C for 20 min. Finally the chip was exposed to O_2 plasma treatment ($P = 400$ W, $t = 4$ min) to remove the residues of solvent and all organic ligands of the metal particles. Similar drop coating method was applied for the formation of non-doped reference layers [24]. In order to estimate the nano-particle concentration, we calculated with an average WO_3 nano-rod (110 nm diameter and 5 μm length) and metal nano-particles sizes of 29 and 20 nm for Au and Pt, respectively. Considering the original concentrations of WO_3 and noble metals as well as the size of the particles, in the controlled volume drops, the transferred quantity of each component can be calculated. In this work a maximum of 14 metal particles/nano-rod is achievable for both systems.

2.6. Device characterization

Deposited layers were analysed by field emission scanning electron microscopy (FESEM, Zeiss-SMT LEO 1540XB).

Sensors were functionally tested in a dedicated mass flow controlled flow-through type system using synthetic air as ambient. The set flow rates and the geometry of the polished metal components provide laminar flow during tests, thereby enabling pulse like introduction of gases and reliable read-out of sensor response.

3. Results and discussion

The structure of WO_3 nano-rod layers doped with Pt and Au nano-particles is presented in Fig. 1. The measured layer resistance is composed of the parallel and serial resistances of individual nano-rods and their contacts. As the distance of the comb-like electrodes on the hotplate is 10 μm and the characteristic length of the 80–180 nm diameter nano-rods is 4–5 μm, dominant contribution to the layer resistance is attributed to the rods themselves.

The size of metal nano-particles was determined by an independent measurement made on a flat surface. This way an appropriate number of metal particles were formed for statistics (Fig. 1). An average size of 20 nm and 29 nm was determined for Pt and Au, respectively. Note, that these values represent the metal without ligands.

With reference to our previous work [34] the responses of both types doped and bare WO_3 nano-rod layers were measured for NH_3 and H_2S. Similarly to other reports in the literature the best signals were detected for H_2S. All layers exhibit much higher sensitivity for H_2S than for NH_3, whereas very limited effect of doping could be detected in case of NH_3 exposure. Gold doped samples show 22 times higher response for H_2S over NH_3 (Fig. 2). Thereby we focus on hydrogen sulphide in the following sections.

Fig. 3 presents the sensor performance in the temperature range between 140 °C and 300 °C, as measured in 10 ppm H_2S. Continuously increasing sensitivity was found up to 260 °C for all the three type layers, then the signal started to decrease. As we got the same characteristics for all materials, we think that this phenomenon is due to the starting phase transition from the original hexagonal crystal structure to the monoclinic phase. Similar effect was also described in [39] by stepwise heating of