Vertically Aligned WO₃–CuO Core–Shell Nanorod Arrays for Ultrasensitive NH₃ Detection

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Vertically aligned WO₃–CuO core–shell nanorod arrays for NH₃ sensing are prepared. The sensor is fabricated by preparing WO₃–CuO nanorod arrays directly on silicon wafer with interdigital Pt electrodes. The WO₃–CuO nanorod arrays are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The sensor based on the vertically aligned WO₃–CuO nanorod arrays exhibits ultrasensitive NH₃ detection, indicating *p*-type behavior. The optimum sensing temperature is found to be about 150°C. Both response and recovery time to NH₃ ranging from 50 ppm to 500 ppm are around 10–15 s. A possible NH₃ sensing mechanism of the vertically aligned hybrid nanorod arrays is proposed.

Keywords: WO₃–CuO core–shell; nanorod arrays; vertically aligned; heterojunction; NH₃-sensing.

1. Introduction

Toxic gases, such as NH₃, NO₂, CO, H₂S and SO₂, cause adverse impact on living organisms. Among them, NH₃ is one of the most hazardous substances and it is extremely noxious if inhaled above the conservative level (25 ppm) of more than 15 min. Therefore, it is necessary to build up ultrasensitive NH₃ gas sensors with short response and recovery time.

Solid-state resistive-type metal oxide gas sensors (MOGS) have been widely used in gas sensor applications, due to their high sensitivity, low cost, simplicity and the compatibility with modern

electronic devices.^{1–3} In order to obtain great sensing performances of MOGS, one-dimensional (1D) metal oxide nanostructures and 1D heterojunction composite nanostructures^{4,5} have been investigated due to their large surface area, size-dependent properties and the nano-heterojunction effects.³ Vertically aligned ordered 1D arrays effectively avoid the dense stacking of rod monomers, especially, resulting in novel physicochemical characteristics, such as higher gas response and shorter gas recovery.⁶

Among the numerous transition metal oxides, tungsten oxide (WO₃), as a wide bandgap *n*-type

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semiconductor, has received considerable attention in various gas detection, such as NO_x , H_2S , H_2 and NH_3 over the years.^{7–10} Copper oxide (CuO) has the unique property of being intrinsically p -type. In the last decade, p - n heterojunction sensors composed of an n -type metal oxide and CuO were reported to have a good sensitivity to reducing gases owing to the interface between n -metal oxide and CuO .¹¹ Much effort has been focused on the WO_3 -based nanocomposites, such as $\text{WO}_3@Au$,¹² graphene- WO_3 ,¹³ $\text{WO}_3\text{-SnO}_2$,¹⁴ since their synergetic enhancement and heterojunction effects attribute to the enhanced gas sensing properties. However, gas sensors based on 1D $\text{WO}_3\text{-CuO}$ composite structures are limited.^{8,15–17} Additionally, the template or catalyst was usually necessary to synthesize WO_3 -based nanorod arrays in the previous reports, using chemical vapor deposition, electrochemical anodization and hydrothermal approaches.^{8,18,19}

Here, vertically aligned $\text{WO}_3\text{-CuO}$ core-shell nanorod arrays are synthesized using a noncatalytic two-step annealing process of sputtered metal film on silicon wafer. The growth mechanism of the vertically aligned nanorod arrays is discussed. The NH_3 sensing behaviors of the $\text{WO}_3\text{-CuO}$ core-shell arrays at different temperatures are reported. A possible NH_3 sensing mechanism for the hybrid is proposed.

2. Experimental Section

Growth of WO_3 nanowires: W nanowires were prepared through magnetron sputtering followed by annealing in argon atmosphere. First, a pair of interdigitated Pt electrodes with a thick of 100 nm, 6 fingers and gap length of 1.2 mm for gas sensing test were deposited on Si substrates using magnetron sputtering. Second, a W film of thickness ~ 50 nm was deposited on the Si substrate with Pt electrodes by DC magnetron sputtering at room temperature (RT) using a W target (purity 99.999%) in argon atmosphere (purity 99.999%). Then, the as-deposited W film was annealed in argon atmosphere in a tube furnace at 650°C for 1 h. W nanowires were grown on Si substrate. WO_3 nanowires were obtained by annealing W nanowires at 450°C for 1 h in air.

Growth of $\text{WO}_3\text{-CuO}$ core-shell nanorod arrays: To functionalize p - CuO shell on WO_3 nanowires, a Cu film of thickness ~ 5 nm was first deposited on the W nanowires by sputtering a Cu

target. The Cu-deposited W nanowires were subsequently annealed at 450°C for 1 h in air, creating an almost continuous p - CuO nanofilm on n - WO_3 nanowires. The vertically aligned $\text{WO}_3\text{-CuO}$ core-shell nanorod arrays were obtained.

Microstructure observation: X-ray diffraction (XRD, RIGAKU D/MAX 2500 V/PC, $\text{CuK}\alpha$ radiation) was used to investigate the phases and crystalline structures of samples. Field-emission scanning electron microscopy (FESEM, FEI NanoSEM 430 and Hitachi S-4800) and transmission electron microscopy (TEM, Tecnai G2 F20) were employed to examine microstructures.

Sensing measurement: The gas sensing properties of sensors were evaluated in a static gas sensing characterization system consisting of a glass test chamber, a flat heating plate, a programmable digital multimeter and data acquisition system.²⁰ The measuring temperature was controlled by temperature control box. Gas was introduced into the chamber directly to get the desired concentration, and the ambient relative humidity was about 35%. Gas response (R) was evaluated as the ratio of R_g/R_a , where R_a is the resistance in the absence of a target gas and R_g is the resistance measured in the presence of a target gas for reducing gases.

3. Results and Discussion

3.1. Microstructure analysis

Phase identification for WO_3 nanowires and $\text{WO}_3\text{-CuO}$ core-shell nanorods is performed by XRD. As shown in Fig. 1, both the samples exert the same diffraction peaks, which can be good to the

Fig. 1. XRD patterns of (a) control WO_3 nanowires and (b) $\text{WO}_3\text{-CuO}$ core-shell composite.

monoclinic phase of WO₃ (P-1 (No. 2) space group, with typical cell parameters of $a = 7.309$ Å, $b = 7.522$ Å, $c = 7.678$ Å and $\beta = 90.92^\circ$; ICDD card No. 71-0305). Meanwhile, the intense diffraction peak at $2\theta = 23.259^\circ$ suggests that WO₃ for both samples is strongly oriented in (002) direction. However, no obvious characteristic peaks in accordance with CuO are observed in the pattern recorded from the WO₃-CuO core-shell sample. This may be due to the thin CuO shell, which is difficult to identify by using the conventional XRD method.

W nanowires, as shown in Fig. 2(a), were obtained from W film after annealing in argon atmosphere. The W nanowires in Fig. 2(a) became WO₃ nanowires keeping the 1D nanostructure after the subsequent annealing in air at 450°C for 1 h, as shown in Fig. 2(b). A cross-sectional SEM image of WO₃ nanowires, shown in Fig. 2(c), clearly demonstrates the connection of the nanowires. Diameters of the WO₃ nanowires range from 10 nm to 20 nm, and their lengths range from 100 nm to 200 nm. Further nanostructural analysis was done by TEM. Figure 2(d) presents a low magnification TEM image of high density WO₃ nanowires. The measured spacing between the fringes in the lattice is approximately 0.38 nm [Fig. 2(e)], which matches

well with the (002) d -spacing for the WO₃ nanowires, supporting the XRD pattern of WO₃ nanowires. The selected area of electron diffraction pattern obtained from a region of the WO₃ nanowires [inset of Fig. 2(e)] shows sharp diffraction spots, confirming single crystallinity of the WO₃.

From the above description, the formation of W nanowires is the key process for the present work. The growth mechanism of W nanowires obtained from annealing W film is suggested to the stress, that is consistent with the previous reports.^{21,22} The sputter deposited W film has an intrinsic residual stress, which provides one of the control factors for producing high dense W nanowires during the heating process in Ar ambience.

The vertically aligned WO₃-CuO core-shell nanorod arrays were prepared by two-step sputtering and subsequent annealing treatment method. A plane-view SEM image of the WO₃-CuO nanorod arrays is shown in Fig. 3(a). Cross-sectional SEM image shows the vertically aligned nanorod arrays of the hybrid [Fig. 3(b)]. Almost continuous granular film attached to the surface of WO₃ nanowire observed by TEM is shown in Fig. 3(c). The granular film is identified as CuO in the high-resolution TEM image as shown in Fig. 3(d). Lattice fringes, not only from WO₃ but also from CuO, are clearly

Fig. 2. SEM of (a) W nanowires and (b) WO₃ nanowires. (c) cross-sectional SEM of WO₃ nanowires in (b). (d) low-magnification TEM image of some WO₃ nanowires. (e) high-resolution TEM image of WO₃ nanowire showing the lattice fringes. The inset of (e) presents a selected area of electron diffraction pattern.

Fig. 3. SEM images of WO_3 -CuO core-shell: (a) plane view and (b) cross-section. Typical TEM images of WO_3 -CuO: (c) low magnification and (d) high magnification.

shown. The fringe patterns with interspacing distances of 0.232 nm, 0.231 nm, 0.252 nm and 0.186 nm are similar to the interplanar distances of the (111), (200), (002) and (-202) lattice planes of CuO, respectively (ICCD card No. 89-5899). The lattice spacing of WO_3 is 0.38 nm, matching well with its (002) d -spacing, which is consistent with results of the control WO_3 nanowires shown in Fig. 2(e). Notably, the interface between WO_3 and CuO appears clearly, without considerable interdiffusion, which is suggestion of an abrupt WO_3 -CuO heterojunction interface. Obviously, WO_3 keeps its crystallinity and 1D nanostructure, after covered by the CuO shell.

3.2. Gas-response properties

Figure 4(a) shows the schematic illustration of the gas sensor device with a pair of interdigitated Pt electrodes based on the vertically aligned WO_3 -CuO core-shell nanorod arrays. Since the interconnections of the WO_3 -CuO core-shell nanorod

Fig. 4. (a) Schematic illustration of the gas sensor device based on the hybrid nanorod arrays.

monomers, as shown in Fig. 3(b), the interdigitated Pt electrodes are efficient for gas sensing measurements of the sensor device.

Operating temperature has a significant influence on the sensor's gas response. Figure 4(b) shows the temperature dependence of the response to 500 ppm NH₃ of the WO₃-CuO hybrid sample, with the temperature ranging from RT 25°C to 200°C. Clearly, the hybrid sample shows the largest response to 500 ppm NH₃ at 150°C. On the basis of this result, all the other sensing measurements are performed at 150°C.

The real-time response of the hybrid sample to varied concentrations of NH₃ decreasing from 500 ppm to 50 ppm at 150°C is shown in Fig. 4(c). The resistance of the WO₃-CuO hybrid increases upon exposure to NH₃, consistent with *p*-type semiconductor behavior. Figure 4(d) shows the response of the hybrid sample increasing with increasing NH₃ concentration at 150°C. Using the baseline noise level and the conventional signal-to-noise ratio of 3 implies a limit of detection of 5.6 ppm for NH₃. The response and recovery times range from 10 s to 15 s for all NH₃ concentrations. Figure 4(e) shows the response time and recovery time to 100 ppm NH₃ which is 15 s and 13 s, respectively. The NH₃ sensing performances of WO₃-CuO core-shell nanorod arrays in this paper are much better than that of WO₃ nanorod arrays.²³

Sensing performances of the WO₃-CuO core-shell nanorod arrays-based gas sensor: (b) response to 500 ppm NH₃ at different temperatures (50°C, 100°C, 150°C and 200°C), with the error bars representing the standard deviation of sensitivity of the three exposures to 500 ppm NH₃ at a measured temperature; (c) resistance versus time to 50–500 ppm NH₃ at 150°C; (d) the related response versus NH₃ concentration at 150°C, with the error bars representing the standard deviation of sensitivity of the three exposures to a given NH₃ concentration; (e) the response and recovery time to 100 ppm NH₃ at 150°C.

These phenomena are associated with the *p-n* heterojunctions established between *p*-CuO shell and *n*-WO₃ core in the nanostructure, as shown schematically in Fig. 5. When *n*-WO₃ contacts *p*-CuO, similar to the reports for *p*-CuO/*n*-ZnO heterojunction nanorods²⁴ and ZnO-Cr₂O₃ heteronanostructures,²⁵ electrons transfer from the WO₃ side to the CuO side and holes transfer from the CuO side to the WO₃ side until the Fermi energy levels (E_f) of the two materials become equal because the E_f of WO₃ is higher than that of CuO. The depletion layers are created near the interface on both the CuO and WO₃ sides causing a narrow conduction channel. Thus, a small change in charge carrier concentration can lead to a high variation in sensor resistance. When exposed to NH₃ gas,

Fig. 5. The formation of the *p-n* heterojunction for WO₃-CuO core-shell nanorods: bandgap energy of WO₃ = 2.6 eV and bandgap energy of CuO = 1.35 eV. The energy band diagram is not drawn to scale.

the n -WO₃- p -CuO core-shell nanorods show ultra-sensing performances. Meanwhile, the vertically aligned arrays are helpful for the desorption of NH₃ from the hybrid material, when NH₃ is off. The similar mechanism has also been reported on other pollutants detection with nanomaterial-based sensors, such as the modified multi-walled carbon nanotubes/gold nanoparticles could provide a large surface area and good charge-transport capacity to dramatically improve the DNA sensor performance.⁵

4. Conclusion

We have experimentally demonstrated the vertically aligned WO₃-CuO core-shell nanorod arrays for ultrasensitive NH₃ sensing. The vertically aligned nanorod arrays were prepared using a non-catalytic two-step annealing process of sputtered metal films on silicon wafer. The ultrasensitive NH₃ detection was obtained at the optimum temperature of 150°C, with the response and recovery time of 15 s and 13 s, respectively, to 100 ppm NH₃. The excellent NH₃ sensing performances of the hybrid sensor are attributed to the p - n heterojunctions formed between n -WO₃ and p -CuO, as well as the vertically aligned nanorod arrays. This work provides a facile construction route of WO₃-based gas sensing materials, which can be used for NH₃ sensors with high performances.

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