Dip-coating decoration of Ag_{2}O nanoparticles on SnO_{2} nanowires for high-performance H_{2}S gas sensors

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SnO_{2} nanowires (NWs) are used in gas sensors, but their response to highly toxic gas H_{2}S is low. Thus, their performance toward the effective detection of low-level H_{2}S in air should be improved for environmental-pollution control and monitoring. Herein, Ag_{2}O nanoparticle decorated SnO_{2} NWs were prepared by a simple on-chip growth and subsequent dip-coating method. The amount of decorated Ag_{2}O nanoparticles on the surface of SnO_{2} NWs was modified by changing the concentration of AgNO_{3} solution and/or dipping times. Gas-sensing measurements were conducted at various working temperatures (200–400 °C) toward different H_{2}S concentrations ranging within 0.1–1 ppm. The selectivity of Ag_{2}O-decorated SnO_{2} NW sensors for ammonia and hydrogen gases was tested. Results confirmed that the Ag_{2}O-decorated SnO_{2} NW sensors had excellent response, selectivity, and reproducibility. The gas-sensing mechanism was interpreted under the light of energy-band bending by sulfuration, which converted the p–n junction into n–n, thereby significantly enhancing the sensing performance.

1. Introduction

Air pollution caused by H_{2}S gas is extremely dangerous even at low concentrations (sub-ppm level) because this gas is colorless, flammable, and highly toxic. The sources of H_{2}S are very diverse because it can be produced naturally from crude petroleum, oil drilling, and volcano eruption or from the bacterial decomposition of organic matter in anaerobic environments. H_{2}S is also produced as a by-product in biogas plants during waste treatment. The effects of H_{2}S on the human body are summarized in Table 1. The threshold odor concentration of H_{2}S is about 10 ppb, but its toxic concentration range is very broad (i.e., from ppb to ppm). The threshold limit of H_{2}S is reportedly 0.003 ppm for 8 h of exposure. However, the permissible concentration of H_{2}S recommended by the Scientific Advisory Board on Toxic Air Pollutants (USA) ranges within 20–100 ppb. Thus, effective gas sensors for detecting low levels of H_{2}S under field conditions are urgent to develop.

Many techniques for H_{2}S detection have been developed, but metal oxide-based resistive-type gas sensors are advantageous because of their low cost, high sensitivity, real-time detection, portability, and low power consumption. SnO_{2} (ref. 11) is one of the most popular materials for such sensors because of its relatively high sensitivity to various gases, as well as its feasibility in functionalization to improve sensing performance. However, SnO_{2} has the main drawback of low response to low concentration of H_{2}S and poor selectivity over air-polluting gases such as NH_{3}, H_{2}S, and CO. This problem can be solved by using heterojunctions between two dissimilar semi-conducting materials, which utilizes the unique effects and leads to enhanced sensor performance. Nano-heterostructures are often utilized owing to their small size and high surface-to-volume ratio, and many efforts have been devoted to the fabrication of p–n heterojunctions for increasing H_{2}S-sensing performance. The most common p-type metal oxides used to form heterojunctions with n-type SnO_{2} semiconductor are CuO, NiO, and Co_{3}O_{4} (ref. 24) because of their easy sulfidation into CuS, NiS, and CoS, respectively. However, sensors with these oxides can detect H_{2}S gas only at high concentrations of >10 ppm because the sulfidation of transition-metal oxides requires a high supply of sulfur source. Meanwhile, Ag_{2}O has unique characteristics that enable it to functionalize SnO_{2} nanomaterials to enhance gas-sensing performance to different gases such as H_{2}, ethanol, and CO. The decoration of p-type Ag_{2}O on the surface of n-type SnO_{2} is advantage over the use of metallic Ag because it forms the p–n heterojunction, thus enhances the gas sensing performance. Ag_{2}O is also reported easily converted into Ag_{2}S in the presence of H_{2}S because of its low free Gibbs energy for the reaction. The free Gibbs energy for conversion of Ag_{2}O, CuO, and NiO into Ag_{2}S,
CuS, and NiS in the presence of H₂S gas is −224.7, −119.1, and −62.5 kJ mol⁻¹, respectively. Therefore, decoration of Ag₂O nanoparticles on the surface of SnO₂ is expected to show better sensing performance such as low detection limit of H₂S with higher sensitivity than others. However, few studies have focused on improving of H₂S-sensing properties using Ag₂O/ SnO₂ thin film. It is hard to find the related work reported on the decoration of Ag₂O on the surface of SnO₂ NWs for enhanced H₂S gas despite the significantly higher stability of NWs than their thin-film counterparts. Doped thick films have shown good sensitivity to low concentrations of H₂S but are not feasible to miniaturize. Decorated thin films present poor response to high concentrations of H₂S. A previous work has reported extremely low response (99%) to the high H₂S

| Concentration (ppm) | Effects                                      |
|---------------------|----------------------------------------------|
| 0.003–0.02          | Approximate threshold for odor               |
| 3–10                | Obvious offensive odor                       |
| 50–100              | Serious eye irritation and respiratory tract irritation |
| 100–200             | Loss of smell                                |
| 250–500             | Fluid buildup in lungs and imminent threat to life |
| 50                  | Anxiety, headache, dizziness, excessively rapid respiration, amnesia, and unconsciousness |
| 500–1000            | Immediate collapse, irregular heartbeat, neural paralysis, and respiratory paralysis leading to death |

Scheme 1. Sensor fabrication process: (A) CVD system used to grow SnO₂ NWs, (B) photo of sensor chips; (C) SnO₂ NW sensor after fabrication.
concentration of 50 ppm at 74 °C. Our group has recently reported the H2S-sensing characteristics of self-heated Ag-coated SnO2 NWs, where the decoration of Ag is realized by sputtering method. However, this method requires vacuum conditions and expensive equipment for Ag decoration, and the content of Ag2O nanoparticles on the surface of SnO2 NWs are difficult to control. Thus, a low-cost, suitable, and effective method for functionalizing p-type Ag2O nanoparticles with low activation energy for reversible sulfidation and oxidation, as well as enhanced H2S-sensing performance of SnO2 NWs, must be developed.

Herein, we reported the dip-coating decoration of Ag2O nanoparticles on the surface of on-chip-grown SnO2 NWs to enhance their H2S gas-sensing performance. Decoration was realized by dipping the sensor in AgNO3 solution, followed by oxidation to form Ag2O nanocrystals on the surface of SnO2 NWs. The effects of Ag2O content on the H2S gas-sensing performance of the SnO2 NWs were studied to maximize sensor response to H2S. Results demonstrated that the sensors processed excellent performance for monitoring extremely low H2S concentrations. The H2S gas-sensing mechanism of the SnO2 NWs functionalized with Ag2O nanoparticles was also discussed through the perspective of band-structure and sulfuration process.

2. Experimental

The preparation of SnO2 NWs-based sensors has been described in our previous publication. The NW sensors were directly grown on thermally oxidized silicon substrate using a chemical vapor deposition system, as shown in Scheme 1(A). In a typical procedure, SnO2 NWs were grown on seeded Pt electrodes at 750 °C from a starting material of Sn powder through thermal evaporation. Growth proceeded at 750 °C for 20 min with an oxygen gas flow of 0.5 scm and pressure of 1.8 × 10⁻¹ torr. For one batch of fabrication, up to 8 samples were obtained, as shown in Scheme 1(B). The SnO2 NWs were homogenously grown on the Pt electrode fingers, as shown in Scheme 1(C). The bare SnO2 NWs sensors were decorated with Ag2O nanoparticles by dip coating in AgNO3 solutions and subsequent annealing at 500 °C for 3 h in air. This decoration method had the advantage over the sputtering method of not requiring vacuum conditions. The density of Ag2O nanoparticles decorated on the surface of SnO2 NWs was controlled by varying the concentration of AgNO3 solution (0.05, 0.2, and 1 mM) and the dipping times (1, 5, and 20 times). The samples were denoted as S0, S1, S2, S3, S4, and S5 (Table 2). The morphology, chemical composition and structural characteristics of pristine and Ag2O-decorated SnO2 NWs were investigated by scanning electron microscopy (SEM; JEOL 7600F), energy-dispersive X-ray spectroscopy (EDS), high-resolution transmission electron microscopy (HRTEM; JEOL 2100F), and X-ray diffraction (XRD; D8 Advance).

Gas-sensing properties were measured using a SourceMeter® Keithley 2602B. Details about the gas-sensing measurement system are described elsewhere. Dry air was used as reference and diluting gas. Sensor response to different H2S concentrations (0.1–1 ppm) at various working temperatures (200, 250, 300, 350, and 400 °C) were investigated. The selectivity among reducing gases (including ammonia and hydrogen) and the reproducibility of the sensors were also tested. During gas-sensing measurements, sensor resistance was continuously recorded, and the target gas and dry air were alternatively switched on/off. Gas response was defined as $S = R_a/R_g$ for the reducing gas H2S, where $R_a$ and $R_g$ are the sensor resistances in air and in target gas, respectively.

3. Results and discussion

3.1. Material characterization

We did not characterize all samples and instead selected sensors S1, S2, and S5 for SEM, EDS, and TEM analysis. Fig. 1(A) illustrates a SEM image of SnO2 NWs (S1) grown on patterned Pt electrodes. Notably, the electrode finger was 20 μm wide [inset of Fig. 1(A)]. Although the gap between two electrode fingers was 20 μm, the grown SnO2 NWs can still efficiently cover the gaps, as shown in the inset of Fig. 1(A). SnO2 NWs grew primarily on the surface of Pt electrode fingers, but their lengths were controlled sufficiently to connect between the fingers and thus act as conducting channels in the gas-sensing measurement. The average diameter of SnO2 NWs was approximately 70 nm. The surface of pristine SnO2 NWs was as smooth as that of the single crystal. This result was consistent with the growth of SnO2 NWs by vapor–liquid–solid mechanism. Herein, we did not use Au as catalyst during the growth of SnO2 NWs, so belt-like NWs were obtained at the initial state. A SnO2 NW comprises a single crystal, as reported in our previous article. Composition analysis of the SnO2 NW by EDS [Fig. 1(B)] revealed the existence of O, Sn, and Pt elements. Pt was originally from the electrode, whereas O and Sn were from the SnO2 NWs.

The SEM image of SnO2 NWs after decoration with Ag2O nanoparticles (S2) is presented in Fig. 1(C), whose inset is a low-magnification SEM image. The electrode fingers were covered by the SnO2 NWs. Ag2O decoration by dip coating maintained the morphology of the SnO2 NWs, but their surface was not as smooth as that of the pristine sample and tiny particles can be seen in the SEM images. The high-magnification SEM image revealed the presence of Ag2O nanoparticles on the surface of SnO2 NWs. EDS composition analysis of S2 [Fig. 1(D)] confirmed the presence of Ag at an energy of 2.98 eV despite the quantitative evaluation displaying a value of zero.
The SEM image of S5 is shown in Fig. 1(E), whose inset is a low-magnification SEM image of S5. With increased AgNO₃ amount in dipping solution and dipping times, the morphology of the SnO₂ NWs slightly changed. More tiny particles can be seen in the SEM image of S5, but the sample maintained its entangled NW morphology. Whether the Ag₂O nanoparticles continuously or discontinuously decorated the surface of SnO₂ NWs was difficult to observe simply by SEM observation. However, the surface of the samples was found to have increased roughness with increased Ag₂O decoration. EDS composition analysis of S5 [Fig. 1(F)] showed that the content of Ag was very high (about 3.5 wt%). This result demonstrated that increasing the concentration of AgNO₃ solution and the dipping times can increase the content of Ag₂O nanoparticles decorated on the surface of SnO₂ NWs for effective H₂S detection.

To further study the decoration of Ag₂O on the surface of SnO₂ NWs, we selected S1, S2, and S5 for TEM characterizations. The grown SnO₂ NWs had a very smooth and clean surface [Fig. 2(A)]. The average diameter of a SnO₂ NW was approximately 70 nm, consistently with the observation by SEM images. No Ag₂O nanoparticle was observed in this sample possibly because the AgNO₃ concentration of the dipping solution was too low. The HRTEM images of S2 and S5 are shown in Fig. 2(B), and (C), respectively. The black dots decorated on the SnO₂ NWs surface were Ag₂O nanoparticles. Given that S2 was decorated by a low concentration of AgNO₃ (0.2 mM) solution, the density of Ag₂O nanoparticles on the surface of SnO₂ NWs was very low [Fig. 2(B)] and the particle sizes were about 7 nm. The size and density of Ag₂O increased with increased AgNO₃ concentration (1 mM, 20 times of dipping), as observed in S5 [Fig. 2(C)]. The diameter of Ag₂O nanoparticles decorated on the surface of SnO₂ NWs ranged within 5–20 nm. However, they were still smaller than the diameter of SnO₂ NWs. The wettability of AgNO₃ solution on the SnO₂ NW surface is very important for the decoration of Ag₂O nanoparticles performed by dipping method. Wettability ensures the homogenous decoration of Ag₂O nanoparticles on the total surface of SnO₂ NWs. At a high density, Ag₂O particles may agglomerate and form a large cluster. A high-magnification HRTEM image of about 5 nm Ag₂O nanoparticle is shown in Fig. 2(D). The interspacing of ~0.23 nm, which corresponded to the (200) lattice plane of cubic structured Ag₂O, was observed. This result was consistent with a previous one on the thermal decomposition of AgNO₃ at 250–440 °C (ref. 43) into Ag. Then, Ag was oxidized into Ag₂O at an oxidation temperature of about 350–500 °C. In the process of e-beam decoration, Ag nanoparticles are anisotropically decorated on one side of NWs but not homogeneously. Herein, the wet chemical method was used to ensure...
that nanoparticles were homogenously decorated on the surface of the NWs. Notably, S5 had larger Ag$_2$O nanoparticles than S2, but decoration was not continuous because overdecoration of Ag$_2$O nanoparticles can reduce sensor response.

### 3.2. Gas-sensing characteristics

Fig. 3(A)–(F) show the changes in transient resistance with time of S0–S5, respectively, upon exposure to various H$_2$S concentrations (0.1, 0.25, 0.5, and 1 ppm) measured at different working temperatures (200, 250, 300, 350, and 400 °C). S0 showed significant response to H$_2$S at all measured temperatures, but the response and recovery times were very long at low working temperature [Fig. 3(A)]. At a working temperature of 200 °C, S0 required almost 1.5 h to finish one measurement at four concentrations of H$_2$S. Thus, stair-type tests were conducted for H$_2$S gas sensing because of the slow recovery characteristics [Fig. 3(B)–(F)]. This finding indicated that measurements were conducted through a stepwise increase in H$_2$S concentration from 0.1 ppm to 1 ppm before finally being refreshed by dry air. The obtained plots illustrated that the resistance of pristine and decorated SnO$_2$ NW sensors steeply increased when H$_2$S gas was injected into the test chamber [Fig. 3(B)–(F)]. The resistance then recovered to the initial values when H$_2$S was replaced by dry air. All these sensors presented the typical n-type gas-sensing behavior of SnO$_2$ NW semiconductor, where resistance decreased with increased H$_2$S gas exposure. The base resistance in air of pristine SnO$_2$ NWs (S0) was much smaller than that of Ag$_2$O-decorated SnO$_2$ sensors from S1 to S5. S5, with the largest amount of Ag$_2$O decoration, had the highest resistance values in air of about 7 MΩ at 200 °C. Notably, Ag$_2$O is also a good conductor, so the high base resistance value of S5 confirmed that the nanoparticles decorated on the surface of SnO$_2$ NW formed the p–n heterojunction. Based on the plot of transient resistance versus time of the sensors, we roughly estimated that the response values increased but the recovery rate of the sensors decreased with increased Ag$_2$O decoration.

The quantitative response values of different sensors are shown in Fig. 4(A)–(F). The response values of all sensors decreased with increased working temperature within the measured range. This result was similar to that of other metal-oxide-based H$_2$S gas sensors. The pristine SnO$_2$ NW sensor (S0) had the highest response value of less than 4 over all the range of working temperatures and gas concentrations [Fig. 4(A)]. The response values for 1 ppm H$_2$S decreased almost linearly from 3.6 to 2.9 with increased working temperature.
from 200 °C to 400 °C. These values were very low compared with the response of Ag_2O-decorated SnO_2 NW sensors [Fig. 4(B)–(F)]. The responses of Ag_2O-decorated SnO_2 NW sensors from S1 to S5 were much higher than that of pristine SnO_2 NWs, S0. The responses of Ag_2O-decorated SnO_2 NW sensors increased with increased amount of decorated Ag_2O nanoparticles. All sensors showed better response at lower operating temperatures, reaching the highest values at 200 °C within the measured range. The response values to 1 ppm H_2S at 200 °C of S1–S5 were approximately 61, 358, 392, 690 and 1155, respectively. The response to 1 ppm H_2S at 200 °C of S5 was about 320-fold higher than that of S0 under the same measurement condition. Notably, the maximum response to 1 ppm H_2S gas of rGO-loaded Fe_2O_3 nanofibers is only 9.2. Herein, all sensors had decreased response values with increased working temperature from 200 °C to 400 °C. The response to 0.1 ppm H_2S at 400 °C of S1 was 2.5, whereas that of S5 was much higher at about 16. Clearly, within the studied H_2S
concentration range (0.1–1 ppm), S5 had the best sensing performance because of its high sensitivity. This finding can be attributed to the p–n heterojunctions between Ag$_2$O nanoparticles on the surface and SnO$_2$ NWs, similar to the p–n heterojunctions between CuO and SnO$_2$ (ref. 19) or NiO and SnO$_2$. Details about the gas-sensing mechanism are discussed in subsequent sections.

The response values of different sensors measured at 200 °C as a function of H$_2$S concentration are shown in Fig. 5(A). With a low content of Ag$_2$O decoration (S0 to S4), the response values increased almost linearly with H$_2$S concentration in the

Fig. 4 Response to different H$_2$S concentrations various working temperature of the sample: S0 (A), S1 (B), S2 (C), S3 (D), S4 (E), S5 (F).
measured range, but their values were low. The highest response value of the sensor S0 at 200 °C for 1 ppm H₂S is about 3.7. S5 had the highest response values, and the response values increased nonlinearly with H₂S concentration. Along with the gas response, the recovery time of the sensor is very important in practical applications because it determines sensor reusability. The effects of working temperature on the recovery time of Ag₂O-decorated SnO₂ NW sensor are shown in Fig. 5(B). Obviously, the sensor had very poor recovery characteristics at low working temperatures of 200, 250, and 300 °C, i.e., resistance did not recover to the initial value after refreshing for 1000 s. However, the sensor presented 100% recovery characteristics at working temperatures of 350 and 400 °C, with a recovery time of approximately 70 s. In practical application, balance should be achieved between sensor sensitivity and recovery depending on the objective of the application. For instance, the sensors based on 2D materials have poor recovery characteristics, but they could operate at room temperature, thus suitable for low power consumption devices.⁴⁸,⁴⁹ Herein, the long recovery time is possible due to the formation enthalpy of Ag₂S (−32.6 kJ mol⁻¹) is lower than that of Ag₂O (−31 kJ mol⁻¹), thus it requires higher energy to break the bonding of Ag₂S than that of Ag₂O compound. As a result, the sensor has longer recovery time than the response time. The selectivity of S5 toward three reducing gases H₂S, NH₃, and H₂ was tested, and the results are shown in Fig. 5(C). At a low working temperature of 200 °C, the sensor did not show good recovery to H₂S, so we tested the selectivity at 250, 300, 350, and 400 °C. Results demonstrated that S5 had the highest response toward 0.5 ppm H₂S despite the 1000-fold concentration in all working temperatures. At a working temperature of 400 °C, S5 still had a high response value of 44–0.5 ppm H₂S, whereas the corresponding values for 500 ppm NH₃ and 500 ppm H₂ were 1.16 and 11, respectively. Reproducibility and repeatability are also important properties of a gas sensor; thus, we tested the short-term stability of the sensor by switching on/off the ambient from air to 0.25 ppm H₂S gas and back to air at a working temperature of 250 °C. As shown in Fig. 5(D), excepted for the first cycle, the sensor exhibited good recovery characteristics for 10 pulses of measurement, where the base resistance recovered to the initial value after refreshing the chamber with air. The relative standard deviation (RSD) was
calculated by the equation $100 \times S/\bar{x}$, where $S$ is the sample standard deviation, $\bar{x}$ is sample mean. The RSD value of the sensor for ten pulses measurement is 92.4%, indicating the good reproducibility of the device. However, for real application, long term stability of the sensor should be studied. This work will be characterized in next step, and the data will be reported elsewhere.

For a better vision, the H$_2$S sensing performances of the sensors based on functionalized-SnO$_2$ nanomaterials are summarized in Table 3. Compared to other results in the references, our sensor showed comparable working temperature whereas was superior in response toward much lower concentration. This means that the Ag$_2$O decoration on the surface of SnO$_2$ NWs is suitable for development of high performance H$_2$S gas sensor.

### 3.3. Gas-sensing mechanism

The gas-sensing mechanism of a metal oxide-based sensor is determined by the surface reaction of the analyzed gas molecule and pre-adsorbed oxygen species. When SnO$_2$ was exposed to air, atmospheric oxygen molecules were adsorbed on the surface of SnO$_2$ NWs to form oxygen ions ($O_2^-$, $O^-$, and $O^{2-}$) by withdrawing electrons from the conduction band of SnO$_2$, as shown in the following eqn (1)–(3):

$$O_2(gas) + e^- \leftrightarrow O_2^{-(ads)}$$  
$$O_2^- + e^- \leftrightarrow 2O^-$$  
$$O^- + e^- \leftrightarrow O^{2-}$$  

As shown in the above equations, the resistance of SnO$_2$ in air increased because of the formation of a thick conduction-depletion region. When air was replaced by H$_2$S, the oxygen ions reacted with H$_2$S to form SO$_2$ and H$_2$O and then released electrons back to the conduction band, resulting in decreased SnO$_2$ resistance, as presented in eqn (4)–(6):

$$2H_2S + 3O_2^- \leftrightarrow 2SO_2 + 2H_2O + 6e^-$$  

![Energy band diagram of the formation of the p-Ag$_2$O/n-SnO$_2$ junction in air and n-Ag$_2$S/n-SnO$_2$ in H$_2$S atmosphere.](image)

**Table 3** A comparative result on the functionalized-SnO$_2$ gas sensors for H$_2$S detection

| Material              | Conc. (ppm) | Working temp (°C) | Response ($R_{air}/R_{gas}$) | Response/recovery times (s) | Ref. |
|-----------------------|-------------|-------------------|-----------------------------|-----------------------------|------|
| Ag$_2$O–SnO$_2$ thin film | 50          | 74                | 99$^a$                      | >600/4500                    | 35   |
| CuO–SnO$_2$ NWs       | 80          | 300               | 1280                        | 1/828                        | 23   |
| NiO–SnO$_2$ NWs       | 10          | 300               | 1372                        | 11/102                       | 21   |
| CuO–SnO$_2$ NWs       | 10          | 250               | 26.3                        | 180/600                      | 19   |
| CuO–SnO$_2$ nanofibers | 10          | 150               | 3000                        | 2/3000                       | 25   |
| CuO–SnO$_2$ thin film  | 100         | 180               | 25.3                        | 10/42                        | 22   |
| CuO–SnO$_2$ hollow spheres | 1         | 300               | 22.4                        | 500/1000                     | 50   |
| Ag$_2$O–SnO$_2$ mesoporous | 1       | 100               | 71.5                        | 390/1600                     | 33   |
| NiO–SnO$_2$ nanoweb    | 100         | 300               | ~6                          | N/A                          | 26   |
| NiO–SnO$_2$ thin film  | 10          | Room              | 440                         | 2000/30 000                  | 27   |
| Ag$_2$O–SnO$_2$ NWs    | 0.5         | —                 | 21                          | 12/1000                      | 51   |
| SnO$_2$ NWs            | 1           | —                 | ~3.5                        | 50/200                       | 14   |
| Ag$_2$O–SnO$_2$ NWs    | 1           | 200               | 1150 (S5)                   | 350/4000                     | This work |
|                        |             |                   | 60 (S1)                     | 200/1500                     |      |

$^a$ $S = (R_{air} - R_{gas})/R_{air}$. 

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However, the chemophysical processes of decoration with silver and silver oxide involved in the gas-sensing properties of metal oxides can be explained in various ways. The mechanisms are primarily electronic and/or chemical sensitization. The electronic mechanism is related to the extension of the electron-depleted space charge region at the interface between two materials, and the latter is related to the dominance of the dissociation of gas molecules on the surface of decorated materials by spillover effect.

Herein, we believed that the dissociation of gas molecules at Ag-based sites on the surface of Ag-decorated SnO₂ facilitated the charge-transfer reaction between sensor surface and H₂S molecule. The gas-sensing mechanism of Ag₂O-decorated SnO₂ NWs may involve the variation in band structure caused by the conversion of Ag₂O into Ag₂S and back to Ag₂O when the test ambient switched from air to H₂S and back to air, as shown in Fig. 6(A) and (B), respectively. Ag₂O is a p-type narrow band-gap semiconductor (1.3 eV) [57] with a work function of 5.0 eV [55,56] whereas SnO₂ is a n-type wide direct-band-gap (3.7 eV) semiconductor with a higher work function of 4.6 eV. Given the extension of the electron-depleted region underneath Ag₂O nanoparticles on the surface of SnO₂ NWs, the barrier at the interface between these two materials developed much more than usual. Furthermore, the formation of a continuous series of n–p–n junctions by decorating Ag₂O nanoparticles on the network of SnO₂ NWs, which prevented the electron current in SnO₂ NWs, aggravated the decrease in SnO₂ conductivity. Upon exposure to H₂S, Ag₂O was converted into Ag₂S according to eqn (7).

$$\text{Ag}_2\text{O} + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + \text{H}_2\text{O} \quad (7)$$

The conversion of Ag₂O into Ag₂S occurred spontaneously because of the negative free Gibbs energy of the reaction (−224.7 kJ mol⁻¹) at room temperature. Therefore, the conversion Ag₂O into Ag₂S requires less H₂S gas, thus the sensor has a lower detection limit. In addition, Ag₂S can be an n- or p-type semiconductor depending on its surrounding environment and the pressure. The monoclinic α-Ag₂S is a n-type semiconductor with a band gap of ≈1.1 eV and a work function of 4.42 eV. Upon exposure to H₂S, the conversion of p-type Ag₂O into n-type Ag₂S destroyed the p–n junctions of Ag₂O–SnO₂ and formed the n–n of Ag₂S–SnO₂, resulting in largely decreased resistance [Fig. 6(B)]. Ag₂S was then re-oxidized when the sensor was in air and the p–n junctions were re-established, and the sensor resistance thus recovered to its initial value. Hence, the functionalization of silver on the surface of SnO₂ NWs improved their H₂S-sensing properties.

4. Conclusion

We introduced a dip-coating method of decorating Ag₂O nanoparticles on the surface of on-chip-grown SnO₂ NW sensors toward H₂S gas monitoring. The effect of Ag₂O nanoparticles decorated on the surface of SnO₂ NWs on H₂S gas-sensing performance was investigated. SnO₂ NW sensor decorated with Ag₂O nanoparticles illustrated the highest response of 1150 to 1 ppm H₂S at a working temperature of 200 °C with reasonable response and recovery time. Selectivity tests over high concentrations of NH₃ (500 ppm) and H₂ (500 ppm) at various working temperatures presented excellent response, selectivity, and reproducibility, demonstrating the sensor’s potential application in the selective monitoring of low-level H₂S gas. The high performance of the sensor was also confirmed under the light of sulfurlization, which turned the band structure from p–n of Ag₂O–SnO₂ into n–n of Ag₂S–SnO₂.

Conflicts of interest

The authors hereby declare that they have no conflict of interests regarding the publication of this paper.

Acknowledgements

This work was supported by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2017.25.

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