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Short communication

Synthesis of SnO_2 nanowires their structural and H_2 gas sensing properties

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Abstract

SnO_2 nanowires were prepared on bare oxidized silicon, Au and SnO_2-coated substrates by thermal evaporation of tin grains in argon atmosphere at 900 °C. X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM) were used to characterize the SnO_2 nanowires. FE-SEM images indicated that the size of SnO_2 nanowires depend on the type of substrate. Gas sensor was fabricated by dispersing SnO_2 nanowires on an interdigitated Pt-electrode. H_2 gas sensing properties of these sensors made of nanowires prepared on three different substrates were measured at various operating temperatures and concentrations respectively. SnO_2 nanowires deposited on Au-coated substrates showed the highest sensitivity of 11.5 at 100 °C upon exposure to H_2 gas of 1000 ppm.

Keywords: SnO_2; Nanowires; Gas sensor; Hydrogen

1. Introduction

Metal oxide semiconductors have attracted tremendous interest due to their wide variety of optoelectronic applications. Currently, nanostructured metal oxides have emerged an exceptional material and attracted a great deal of interest from researchers. Novel physical properties arising from size reduction are very important for present and future nano-device applications in electronic, optical and sensor fields. Low cost, high sensitivity and reliability of metal oxides are essential in both the fabrication and application of gas sensors. Morphology and crystallographic structure of metal oxides have a great effect on the response of conduct-metric type gas sensors. Nanoscale structures, such as nanobelts, nanowires, and nanorings, were found to show high sensitivity as gas sensors due to the reduction of crystal size [1–5].

Among metal oxide, tin dioxide (SnO_2), is an n-type semiconductor with a wide band gap ($E_g \approx 3.8$ eV), which is extensively used in optoelectronic devices. SnO_2 nanostructures have proven as promising material due to their potential applications in nanosensors. In view of this, much attention has been paid to the synthesis and characterization of SnO_2 nanostructures such as nanoparticles, nanowires and nanobelts etc. [6].

Optimization of the gas sensor parameters, for example grain size, band gap, crystal quality and thickness greatly influences the response and recovery of the sensors. It was shown that deposition parameter control, post deposition treatments, and impurity doping affect physical parameters of the metal oxides. In the case of SnO_2, an increase in pyrolysis temperature during deposition reduces the influence of water vapor on the conductivity of the sensors and, therefore, the influence on the sensor response [7,8]. SnO_2 is one of significant semiconductors used for sensing CO and O_2 gases [9]. Various groups investigated different types SnO_2 nanostructures. Very recently gas sensing properties of SnO_2 hollow spheres have been investigated [10,11]. These hollow spheres and microspheres have high surface area and show

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good sensor response and have potential applications in catalysis. However still sphere-like structures are limited by structural defects, crystallinity, conductivity and sluggish electron transport compared to 1D nanostructures. Beside exceptional crystal quality and high surface-to-volume ratio 1D nanostructures play an essential role for high performance of nanoscale devices. For instance a single SnO_2 ribbon was used to detect NO_2 gas at ppm-level at room temperature under UV light [12]. SnO_2 nanobelts showed excellent sensitivity to H_2 gas at room temperature [13]. SnO_2 nanowires film exhibited both high response and reversibility to ethanol, CO, hydrogen, acetone and other gases [14–16]. In this work, we report fabrication of SnO_2 nanowires by thermal evaporation on three different types of substrate, namely, bare oxidized Si substrates, gold (Au) and SnO_2 thin film coated respectively. The structure of the nanowires was observed by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). H_2 sensing properties nanowires were investigated at different operating temperatures.

2. Experiments

SnO_2 or Au films with a thickness of about 10 nm were deposited on the SiO_2/Si (100) substrates by DC sputtering and vacuum evaporation, respectively. Thus, three different types of substrate (Au, SnO_2 and bare) were used. The apparatus used for fabrication of SnO_2 nanowires is shown in Fig. 1. First, an alumina boat loaded with the substrates on which Sn grains with a diameter of 2–3 mm were placed was introduced in a quartz tube which was inserted into a horizontal tubular furnace. The one end of tube was connected with cylinder and the other end of the tube was kept open. Then, Ar gas was introduced into the quartz tube for 20 min. at a flow rate of 50 ml/min. After the flow rate of Ar gas was increased to 100 ml/min, the electric furnace was heated and kept at 900 °C for 1 h. Finally, the furnace was cooled down naturally to room temperature, and the Ar gas was turned off. Finally whitish wool-like product was obtained around the Sn grains from each type of substrate.

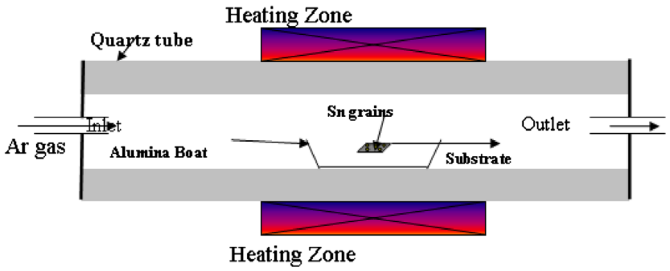

Fig. 1. Schematic diagram of vapor transport tubular furnace used for SnO_2 nanowires synthesis.

The crystallographic structure of the products was investigated by XRD with Cu-Kα radiation using a diffractometer (Shimadzu XRD 6100). The morphology of the products were observed by FE-SEM (JEOL, JSM 6700 F).

Gas sensors were fabricated by dispersing a few drops of SnO_2 nanowires-suspended in an ethanol on oxidized Si substrates with a pair of interdigitated Pt electrodes with a gap length of 0.12 mm. The detailed illustration of SnO_2 gas sensor made of nanowires is shown in Fig. 2. Two sensors for each sample were fabricated. In gas sensing test, the sensors were placed in a quartz tube inserted into an electric furnace. The operating temperature of the sensors was from room temperature (*RT*) to 300 °C. Dry synthetic air mixed with a desired concentration of hydrogen (100–1000 ppm) flowed through the quartz tube at 200 ml/min. The gas flow was controlled with mass flow controller. The resistance of the gas sensors was determined by measuring the electric current when a voltage of 10 V was applied between a pair of Pt electrodes. A computerized Agilent 34970 A multimeter was used for the electrical measurement upon turning the test gases on and off. To determine the selectivity of the prepared sensors to H_2, we chose H_2S and CO gases for practical utilization. At 250 °C when SnO_2 nanowires exposed to H_2S and CO the sensitivity was 0.3 and 0.5 respectively. When 1000 ppm of H_2 gas was introduced the response reached to 2. The much lower response for both H_2S and

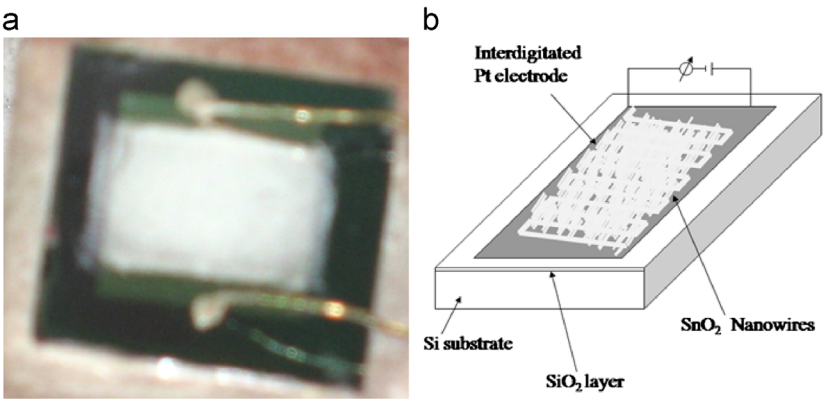

Fig. 2. (a) Photographic image of an electrode and (b) schematic diagram of SnO_2 nanowire based gas sensor device.

CO than that of H_2 implies that the current sensors have very good selectivity towards H_2.

3. Results and discussion

Typical XRD patterns of the as-deposited SnO_2 nanostructures grown at 900 °C are shown in Fig. 3. All the diffraction peaks can be indexed to SnO_2 with a tetragonal rutile structure (JCPDS card No. 41-1445). As shown in Fig. 3, no other peaks are observed in the XRD patterns. This reveals that neither other phases nor Sn metal can be found in the final product.

Fig. 4(a)–(c) show FE-SEM images of the as-deposited SnO_2 nanowires. The inset shows a corresponding high magnification FE-SEM image. The products deposited on the three types of substrate are nanowires/nanobelts. SnO_2 nanowires are about several tens to several hundreds of nanometers in diameter and a few tens of micrometers in length. In addition, the shape of SnO_2 nanowires depends on the type of substrate. The cross section of the nanowires is mostly rectangular for the nanowires deposited on a bare and Au-coated substrate (Fig. 4(a) and (c)). Such rectangular 1D nanostructures are reported in the literature previously by Wang et al. [17]. While the nanowires deposited on SnO_2-coated substrate were generally very thin and resembling with the shape of nanoribbons (Fig. 4(b)). It has been reported by researchers that SnO_2 nanowires and nanobelts were usually formed on bare and Au-coated SiO_2/Si substrates [18,19]. Here, the formation of SnO_2 nanoribbons may be due to the lattice match of substrate which facilitate in seeded nucleation and the grain structure of SnO_2 films prepared by reactive DC magnetron sputtering [20,21]. In this case, Sn atoms evaporated from Sn metal react with oxygen atoms and then the product was probably deposited on the SnO_2 grains. However the growth on Au-coated substrate follow the VLS (vapor liquid solid) mechanism which helps the

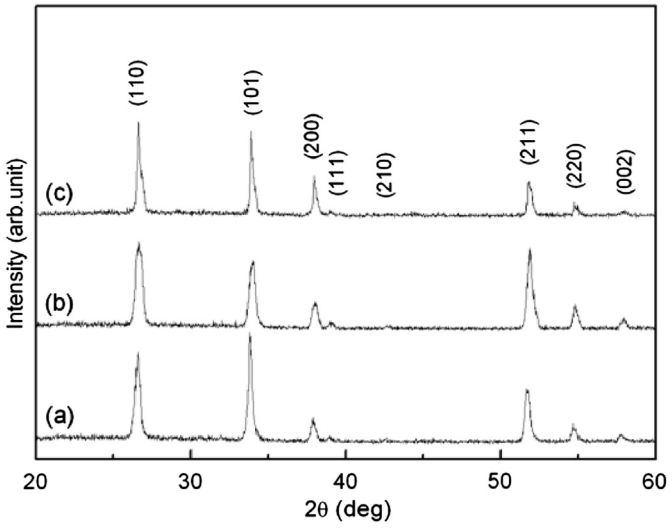

Fig. 3. XRD pattern of SnO_2 nanowires synthesized on (a) bare, (b) SnO_2-coated, and (c) Au-coated SiO_2/Si substrates.

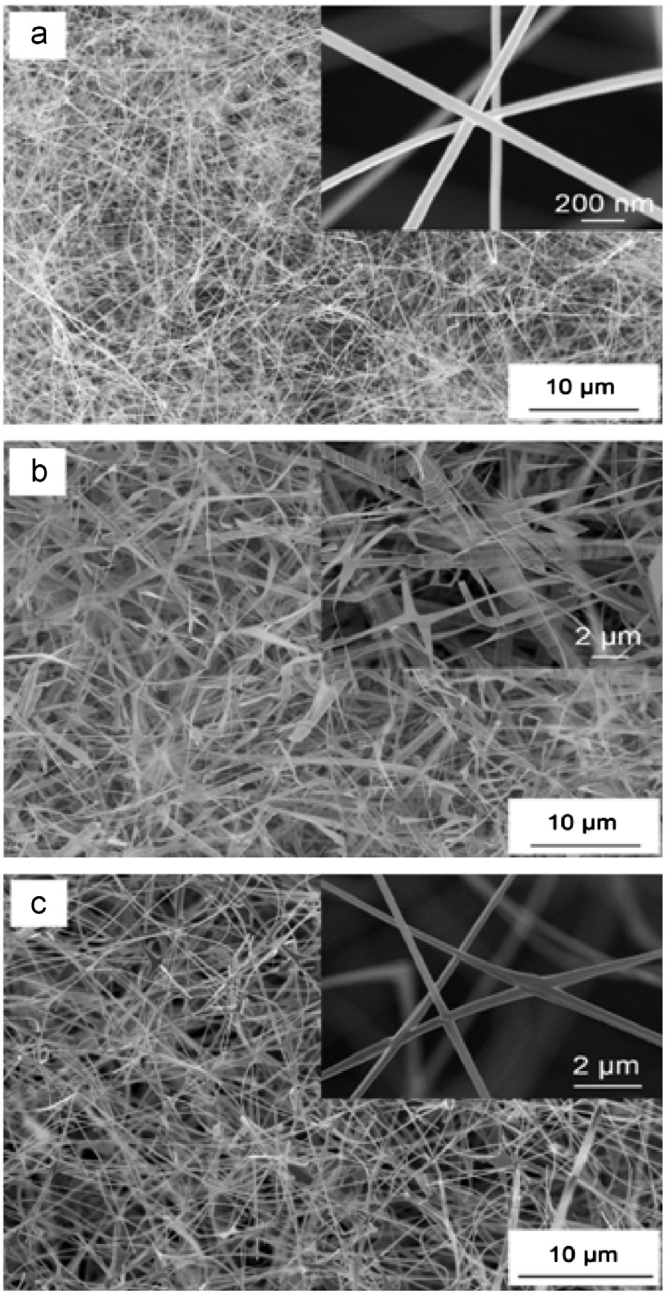

Fig. 4. FE-SEM images of SnO_2 nanowires synthesized on (a) bare, (b) SnO_2-coated, and (c) Au-coated SiO_2/Si substrates.

growth of 1D nanostructures into high aspect ratio. Beside the reaction temperature, flow of gas, surface of the substrate is also important for the growth of 1D nanostructures. Here the surface of the substrate was altered by SnO_2 and Au films which effected on the size and shape of the nanostructures and dimensions remain similar.

The responses of three types of SnO_2 nanowire sensor upon exposure to H_2 at 1000 ppm measured at various operating temperatures are shown in Fig. 5(a)–(c). For all sensors, the resistance measured in air decreased with increasing operating temperature from 50 to 300 °C. When H_2 gas is introduced, the resistance decreases rapidly and saturates within 10 min. The response and recovery time

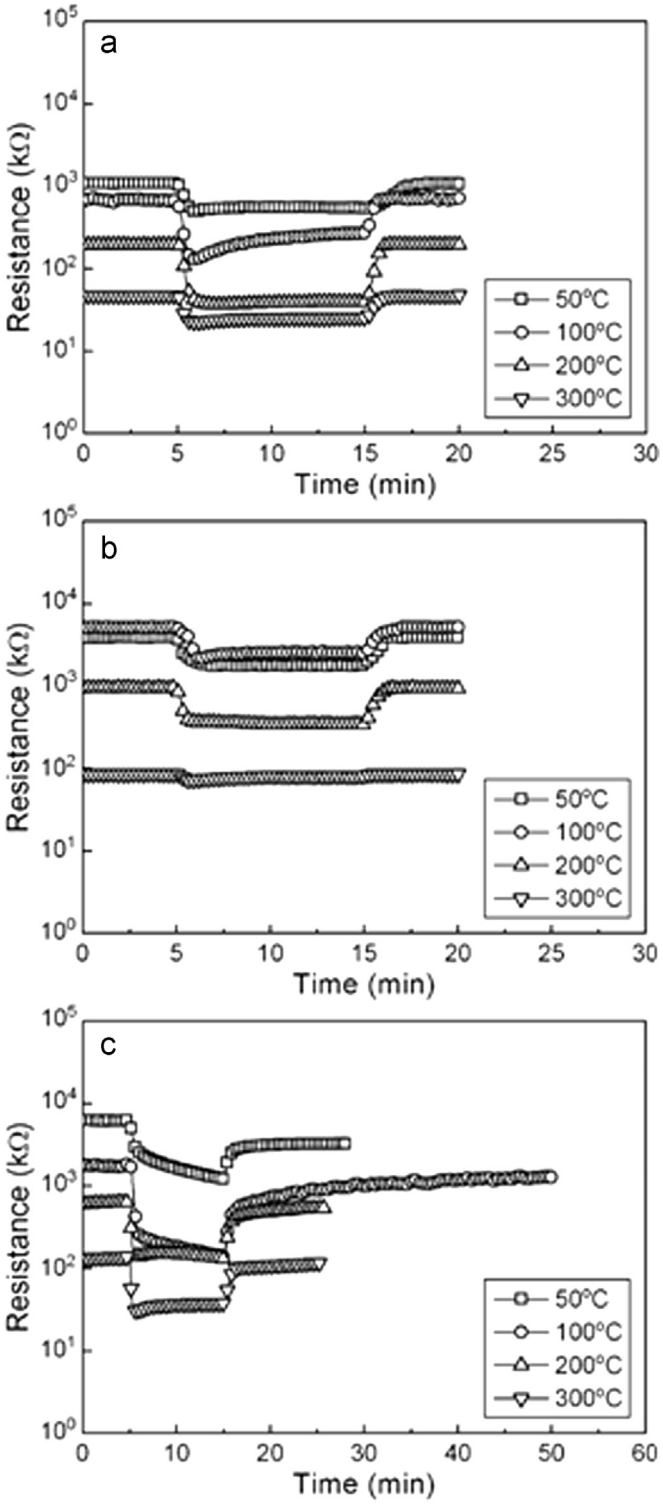

Fig. 5. Changes in the resistance of three types of SnO_2 nanowire gas sensors upon exposure to 1000 ppm H_2 gas at various operating temperatures.

reduces with an increase in operating temperature. The resistance recovers to its initial value after removing H_2 gas, which indicates a good reversibility of these gas sensors. The response of SnO_2 nanowires deposited on Au-coated substrates upon exposure to H_2 gas is greater than that of SnO_2 nanowires deposited on bare or SnO_2-coated substrates.

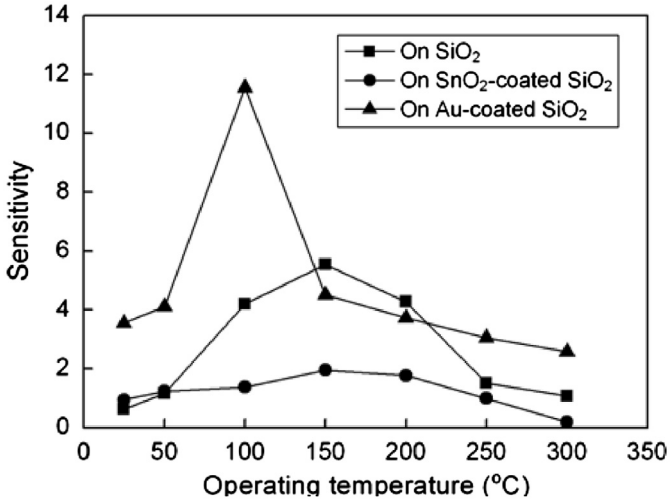

Fig. 6. Sensitivity of three types of SnO_2 nanowires gas sensors upon exposure to 1000 ppm H_2 gas at various operating temperatures.

The sensor sensitivity, defined as $(R_a - R_g)/R_g$, where R_a and R_g are the electrical resistances before and after the introduction of H_2 gas, is shown in Fig. 6 upon exposure to 1000 ppm H_2 as a function of operating temperature for the three different sensors. The sensitivity of SnO_2 nanowires on SnO_2-coated substrates is relatively low, and even the highest sensitivity is 1.96 at an operating temperature of 150 °C. The low sensitivity of this sensor may be attributed to the relatively small surface-to-volume ratio and low conductivity of SnO_2 nanostructures. The sensitivity is higher in the sensor of the bare substrate than the sensor prepared from SnO_2-coated substrate. The maximum sensitivity of 11.5 was obtained for the sensor of the Au-coated substrate at an operating temperature of 100 °C. This value for a pure SnO_2 nanowire sensor is higher than those observed for the SnO_2 nanowire sensor reported elsewhere [15,18]. It is also noticeable that this sensor shows a high sensitivity at a low temperature of 100 °C, which is favorable for lower–power consumption. The synthesis of SnO_2 nanowires on Au-coated substrate follows VLS (vapor solid liquid) growth mechanism [22,23]. The presence of Au on the surface of nanowires may improve the conductivity of nanowires which helps in hydrogen dissociation and trigger the reaction. From these results we can suggest that using nobel metals (Au, Pt, Pd, Ag etc) as catalyst might be helpful for successful growth VLS of nanowires and simultaneously enhance the sensitivity of the metal oxide nanowire based sensors.

Since the dissociation of the H_2 molecules on the surface of the sensor is the first step in the H_2 gas sensing mechanism. The large surface-to-volume ratio of nanostructures also allows more efficient dissociation of H_2 molecules to form atomic hydrogen. Then high accumulation of H_2 atoms on the surface of the sensor takes place. As seen from the FE-SEM images, the nanowires deposited on Au-coated substrates are of high aspect-ratio compared to other substrates. The longer nanowires may be a favorable factor for a change of resistance by chemical

interaction of the gas with the sensing layer. Therefore, the sensitivity is greatly improved.

The changes in the resistance of three types of sensor upon exposure to H_2 gas at 100 °C is shown in Fig. 7. It is clear that the decrease in the resistance of SnO_2 nanowires deposited on SnO_2-coated substrates is relatively small. The decrease in the resistance of SnO_2 nanowires formed on SiO_2/Si substrates is obviously larger than that of the nanowires deposited on SnO_2-coated substrate. As stated earlier the maximal decrease in the resistance upon exposure to H_2 gas was found for SnO_2 nanowires formed on Au-coated substrates. In this case, the resistance does not saturate and still decreases after the introduction of H_2 gas for 10 min. The response times of three types of SnO_2 nanowire gas sensors are less than 2 min. For the nanowires formed on Au-coated substrates, the resistance recovers to its initial value in 30 min after removal of H_2. This long recovery time, compared with the other two sensors, is sufficient and may be attributed to the large decrease in the resistance and the slow desorption of hydrogen atoms from the surface of the nanowires. It is noteworthy to mention that the gas sensing properties were found to be similar and reproducible. Previously we have investigated In_2O_3 and ZnO nanowires, however the stability was not better than SnO_2 [24,25]. Moreover, when the evaluation of the sensor was performed one month later again for the same devices, the results were found reliable. This indicates reasonable stability and durability of the SnO_2 nanowire based sensors.

Fig. 8 shows the dynamic resistance response of SnO_2 nanowires synthesized on bare substrate to H_2 gas at various concentrations (100–1000 ppm) at 150 °C. It can be found that the resistance decreases upon exposure to H_2 gas, and the resistance further decreases with increasing H_2 concentration. The resistance recovers to its initial value after removing H_2 gas, indicating a good reversibility. It should be noted that all sensors show good reversibility at every temperature, irrespective of the type of template. This good reversibility is attributed to the large surface-to-volume ratio of SnO_2 nanowires, making the adsorption and desorption of H_2 gas on the nanowires more simple owing to high chemical reactions.

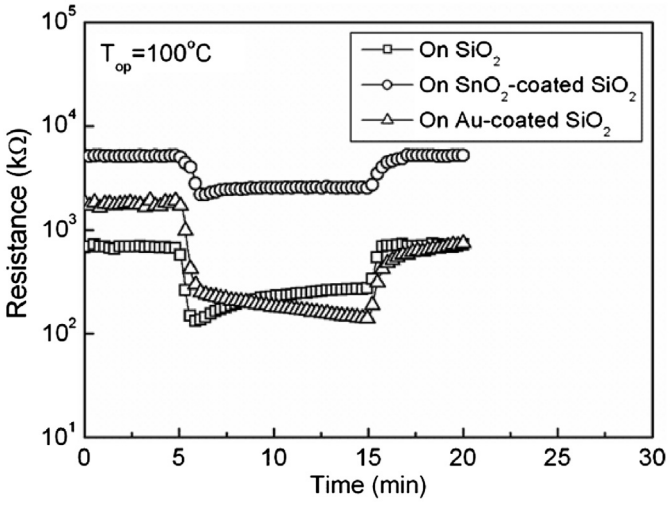

Fig. 7. Changes in the resistance of three types of SnO_2 nanowire gas sensors upon exposure to 1000 ppm H_2 gas at 100 °C.

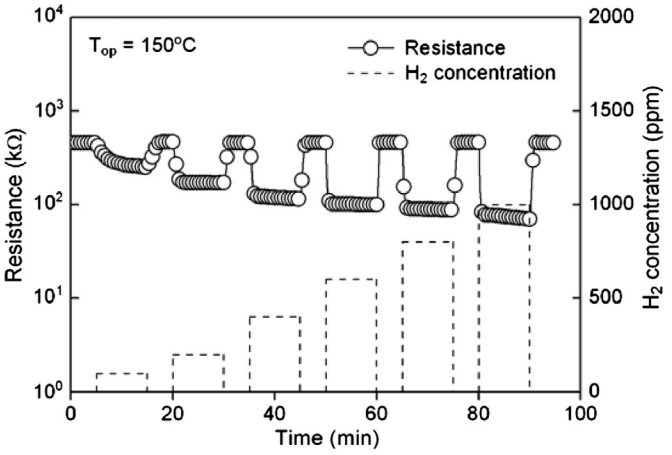

Fig. 8. Dynamic response of the SnO_2 nanowires gas sensor synthesized on bare–SiO_2/Si substrate upon exposure to H_2 gas with various concentrations at 150 °C.

4. Conclusions

SnO_2 nanowires with a tetragonal rutile structure were prepared on bare oxidized silicon Au and SnO_2-coated thin films at 900 °C in argon atmosphere. The size and shape of 1D SnO_2 nanostructures were dependent on the nature of substrate. Rectangular cross section is found for the nanowires prepared on the bare and Au-coated substrates while nanoribbons-like structure is observed on the SnO_2-coated substrate. Gas sensors based on SnO_2 nanowires prepared on different substrates were fabricated. These SnO_2 nanowire gas sensors showed a reversible response to H_2 gas at an operating temperature of RT-300 °C. The highest sensitivity upon exposure to 1000 ppm H_2 gas obtained in this study was 11.54 at 100 °C, which was measured for the SnO_2 nanowires prepared on Au-coated substrates. This sensitivity is high for pure SnO_2 gas sensors.

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References

[1] X.Y. Kong, Y. Ding, R.S. Yang, Z.L. Wang, Single-crystal nanorings formed by epitaxial self-coiling of polar-nanobelts, Science 303 (2004) 1348–1351.

[2] J. Ham, C.M. Leiber, Direct ultrasensitive electrical detection of DNA and DNA sequence variations using nanowires nanosensors, Nano Letters 4 (2004) 51–54.

[3] E. Comini, G. Faglia, G. Sberveglieri, Z. Pan, Z.L Wang, Stable and high-sensitive gas sensors based on semoconducting oxide nanobelts, Applied Physics Letters 81 (2002) 1869–1871.
[4] Z. Li, Y. Chen, X. Li, T.I. Kamins, K. Nauka, R.S. William, Sequence-specific label- free DNA sensors based on silicon nanowires, Nano Letters 4 (2004) 245–247.
[5] N. Yamazoe, New approaches for improving semiconductor gas sensors, Sensors and Actuators B: Chemical 5 (1991) 7–19.
[6] G. Korotcenkov, Metal oxides for solid state gas sensors: what determines our choice, Materials Science and Engineering: B 139 (2007) 1–23.
[7] E. Comini, C. Baratto, G. Faglia, M. Ferroni, A. Vomiero, G. Sberveglieri, Quasi-one dimensional metal oxide semiconductors: preparation, characterization and application as chemical sensors, Progress in Materials Science 54 (2009) 1–67.
[8] A. Kolmakov, X. Chen, M. Moscovits, Functionalizing nanowires with catalytic nanoparticles for gas sensing application, Journal for Nanoscience and Nanotechnology 8 (2008) 111–121.
[9] A. Kolmakov, X.Y. Zhang, G.S. Cheng, M. Moskovits, Detection of CO and O_2 using tin oxide nanowire sensors, Advanced Materials 15 (2003) 997–1000.
[10] J. Zhang, S. Wang, Y. Wang, Y. Wang, B. Zhu, H. Xia, X. Guo, S. Zhang, W. Huang, S. Wu, NO_2 sensing performance of SnO_2 hollow-sphere sensor, Sensors and Actuators B 135 (2009) 610–617.
[11] X. Liu, J. Zhang, X. Guo, S. Wu, S. Wang, Enhanced sensor response of Ni-doped SnO_2 hollow spheres, Sensrs and Actuators B 152 (2011) 162–167.
[12] L.H. Kind, B. Messer, F. Kim, P. Yang, NO_2 photochemical sensing with oxide nanoribbon at room temperature, Angewandte Chemie International Edition 41 (2002) 2405–2407.
[13] L.L. Fields, J.P. Zheng, Room-temperature low-power hydrogen sensor based on a single tin dioxide nanobelt, Applied Physics Letters 88 (2006) 263102–263104.
[14] Y.L. Wang, X.C. Jiang, Y.N. Xia, A Solution-Phase, Precursor route to polycrystalline SnO_2 nanowires that can be used for gas sensing under ambient conditions, Journal of the American Chemical Society 125 (2005) 16176–16177.
[15] D. Wang, X. Chu, M. Gong, Gas-sensing properties of sensors based on single-crystalline SnO2 nanorods prepared by a simple molten-salt method, Sensors and Actuators B 117 (2006) 183–187.
[16] S. Shi, Y. Liu, Y. Chen, J. Zhang, Y. Wang, T. Wang, Ultrahigh ethanol response of SnO_2 nanorods at low working temperature arising from La_2O_3 loading, Sensors and Actuators B 140 (2009) 426.
[17] J.X. Wang, D.F. Liu, X.Q. Yan, H.J. Yuan, L.J. Ci, Z.P. Zhou, Y. Gao, L. Song, L.F. Liu, W.Y. Zhou, G. Wang, S.S. Xie, Growth of SnO_2 nanowires with uniform branched structures, Solid State Communications 130 (2004) 89–94.
[18] Y. Shen, T. Yamazaki, Z.F. Liu, D. Meng, T. Kikuta, N. Nakatani, M. Saito, M. Mori, Microstructure and H_2 gas sensing properties of undoped and Pd-doped SnO_2 nanowires, Sensors and Actuators B, Chemistry 135 (2009) 524–529.
[19] S. Budak, G.X. Miao, M. Ozdemir, K.B. Chetry, A. Gupta, Growth and characterization of single crystalline tin oxide (SnO_2) nanowires, Journal of Crystal Growth 291 (2006) 405–411.
[20] Y.B. Shen, T. Yamazaki, Z.F. Liu, C.J. Jin, T. Kikuta, N. Nakatani, Porous SnO_2, Sputtered films with high H_2 sensitivity at low operation temperature, Thin Solid Films 516 (2008) 5111–5117.
[21] Y.B. Shen, T. Yamazaki, Z.F. Liu, D. Meng, T. Kikuta, N. Nakatani, Influence of effective surface area on gas sensing properties of WO_3 sputtered thin films, Thin Solid Films 517 (2009) 2069–2072.
[22] J.G. Lu, P.C. Chang, Z.Y. Fan, Quasi-one-dimensional metal oxide materials—Synthesis, properties and applications, Materials Science and Engineering R 52 (2006) 49–91.
[23] N. Wang, Y. Cai, R.Q. Zhang, Growth of nanowires, Materials Science and Engineering R 60 (2006) 1–51.
[24] A. Qurashi, E.M. El. Maghraby, T. Yamazaki, T. Kikuta, Catalyst supported growth of In_2O_3 nanostructures and their hydrogen gas sensing properties, Sensors and Actuators, B: Chemical 147 (2010) 48–54.
[25] A. Qurashi, N. Tabet, M. Faiz, T. Yamazaki, Ultra-fast microwave synthesis of ZnO nanowires and their dynamic response to hydrogen gas, Nanoscale Research Letters 4 (2009) 948–951.