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Development of gas sensors based on tungsten oxide nanowires in a metal/SiO_2/metal structure and their sensing responses to NO_2

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Abstract

A gas sensor utilizing self-synthesized tungsten oxide nanowires (TONWs) between two sputter-deposited tungsten carbide electrodes separated by a thin SiO_2 layer, without the use of submicron photolithography process, was proposed. Using a wet etching to the periphery of the SiO_2 layer and a thermal annealing at 750°C in nitrogen, TONWs with $W_{18}O_{49}$(010) crystalline and a typical length and diameter of 0.1.5~0.4 μm and 17~25 nm, respectively, were found linking between the two electrodes. Upon exposure to 2-10 ppm of NO_2 at 160-200 °C, experimental results showed that the proposed TONW gas sensors exhibited quite good sensing properties including high sensitivity, short response and recovery time. Further improvement of the gas sensors sensitivity by a factor of 2.8 ad 3.7 folds has been achieved through a series connection of two and four individual gas sensors.

1. Introduction

Compact solid-state (SS) chemical sensors have been widely used in chemical process control, pollutant monitoring, personal safety and medical diagnosis, etc. Among them, metal oxides (MOs) sensors have been demonstrated with advantages of high sensitivity, low cost, and process compatible with VLSI technology [1]. Essentially, tungsten oxides (TOs) have been shown to be a very high potential candidate because it has an n-type semiconductor properties and a superior responsibility to gases including NH_3, H_2S, NO_2, NO, CO, and H_2 [2-4], etc. However, conventional sensors based on thin films of nano- or poly-crystalline TOs usually exhibit poor performance because carrier transport in these sensors is essentially based on the adsorption and desorption of gas molecular near or at grain boundaries on the surface of the film only. The limited surface-to-volume ratio (SVR) of film type sensors should be one of the obstacles for further enhancing both sensitivity and responsibility for gas detection.

In contrast, nanosized materials such as CNTs, SnO_2 nanowires, In_2O_3 nanowires[5-6], and tungsten–based nanowires (TONWs) [7-8], etc., have attracted lots attention in the fabrication of SS sensors because they have a very high SVR and a good responsibility for chemicals sensing. In recent years, experimental results of nanosensors have been reported and superior characteristics such as high sensitivity, high response speed, and availability for room-temperature operation, etc., have been shown. Nevertheless, utilization of right nano materials with low cost and ease of volume fabrication are still open problems.

In this work, MOs gas sensors using self-synthesis TONWs in a metal/SiO_2/metal sandwich structure was proposed. Key fabrication processes of gas sensors including a side SiO_2 etching and a simple thermal annealing for the growth of TONWs were reported. Gas sensing behaviors of the fabricated devices in responding to NO_2 of various partial pressures at different operation temperatures were presented and discussed. Results obtained from the use of a series connection of the fabricated sensors to improve the sensitivity of the gas sensors were also presented.

2. Experiments

N-type 0.1 Ω-cm <100> Si wafers were used as substrate and a RF sputtering and a PECVD system were employed for the deposition of electrodes and SiO_2 layer, respectively. A WCx (W:C=70:30 wt%) target with a purity of 99.5% was used for the electrode deposition. Figure 1(a) shows schematically the proposed three-layer structure using TONWs as the gas sensing elements. Note that the thickness of the bottom and top electrode were 60 nm and 120 nm, respectively, while the thickness of SiO_2 layer which solely determines the space between the two electrodes without the use of expensive submicron photo lithography technology was of 300 nm. The patterning of the devices was obtained from a reactive ion etching (RIE). A BOE wet etching to the periphery of the SiO_2 layer was conducted first. Then the samples were subjected to a thermal annealing at 750°C in N_2 (60 sccm) ambient for 30 min for the self growth of TONWs [7-8] in the space created by the side etching of SiO_2 layer. Figures 1(b) and 1(c) show the device structure after SiO_2 etching and the growth of TONWs, respectively. It is seen that TONWs with a length in the range of 0.15~0.4 μm firmly link between the top and bottom electrodes.

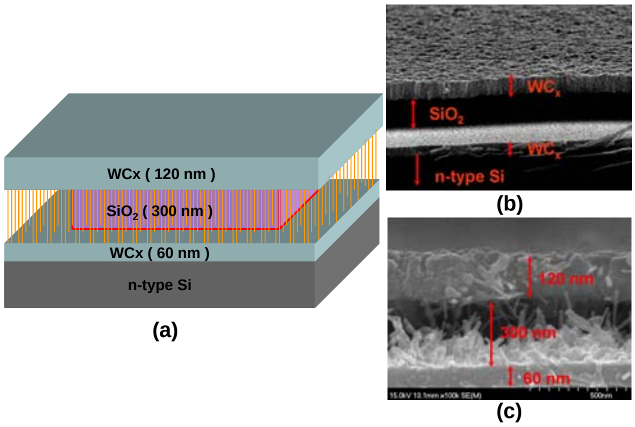

Fig.1 (a) A schematic diagram of the proposed three-layer sensor structure utilizing TONWs as the gas sensing elements. (b) SEM image of the proposed gas sensor after side SiO_2 etching. (c) SEM image of the cross-sectional view of the proposed gas sensor after the self-synthesis of TONWs.

3. Results and discussion

Based on I-V measurement, it is found that the proposed three-layer structure exhibits a current of 2×10^{-10} and 4×10^{-7} A at 2 V before and after thermal annealing, indicating the firm linking of TONWs between the top and bottom electrodes.

Figure 2 shows XRD patterns of the WCx electrodes after thermal annealing in nitrogen for 30 min at different temperatures. For the 750^{o}C-annealed samples, clear (010) peaks were seen which reflects that the main phase of the TONWs is monoclinic $W_{18}O_{49}$. As compared to the stable phase of WO_3, monoclinic $W_{18}O_{49}$ would essentially behave as an n-type semiconductor. Adsorption of oxygen gas related molecular would reduce oxide vacancies in the wires and result in a reduced electron concentration in the conduction band; it thus causes the resistance of TONWs increases with the amount of oxygen adsorption. As compared to the film type sensors, TONWs were expected to exhibit much better sensitivity for gas detection applications because of a higher SVR.

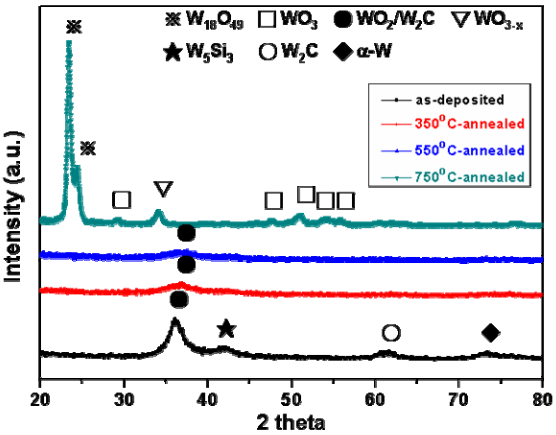

Fig.2 XRD patterns of the WCx electrodes after thermal annealing in nitrogen for 30 min at different temperatures.

In general, gas adsorption of TONWs depends strongly on the working temperature. The influence of the sensitivity of TONWs on the working temperature was shown in Fig. 3(a). During measurement, 100-ppm-NO_2 was introduced into the detection chamber and the temperature of gas sensors was controlled at 160~200^{o}C. By defining the sensitivity of a gas sensor as: $S=R_{gas}/R_{air}$, where R_{gas} and R_{air} are measured resistance of the gas sensor in open air and in the gas environment, respectively, it is found that the sensitivity of the prepared TONWs gas sensors increases with increasing the working temperature. At 200^{o}C (the upper limit of our measurement system), the measured sensitivity of the TONWs gas sensor is only 1.06. Such a low sensitivity might be due to the TONWs in the proposed three-layer structure were in parallel connection between electrodes, hence only the TONW which has the largest diameter and shortest length (i.e., having the lowest resistance) dominates the measured I-V characteristics, under the circumstance, the sensitivity of the parallel connection TOWNs sensor is limited because only a very small amount of gas adsorption would conduct in a single nanowire.

To improve the sensitivity of TONWs sensors, series connection of the proposed sensors by a number 2 and four was also investigated and results were shown in Fig. 3(b)~(c). Note that the content of NO_2 and working temperature were kept at 100-ppm and 200^{o}C, respectively. It was found that the value of S was increased to 2.8 and 3.7, respectively. Good transient response with a pretty short response and recovery time were also obtained.

Transient responsibilities of a series connection of four sensors to NO_2 in the range of 0~10 ppm was shown in Fig. 3(d), in which the measured resistances in air and in NO_2 were about 2 and 2.6 MΩ, respectively. The measured resistances under different NO_2 contents were almost with the same value, indicating that the number of TONWs governing gas sensing is still too small. Nevertheless, it was seen that the proposed device has a good detectability to NO_2 as low as 2 ppm. It is expected that the sensitivity of gas sensors could be further increased through the number of series connections. Gas sensors based on a series connection of TONWs through a large number of patterned WCx islands is now underway.

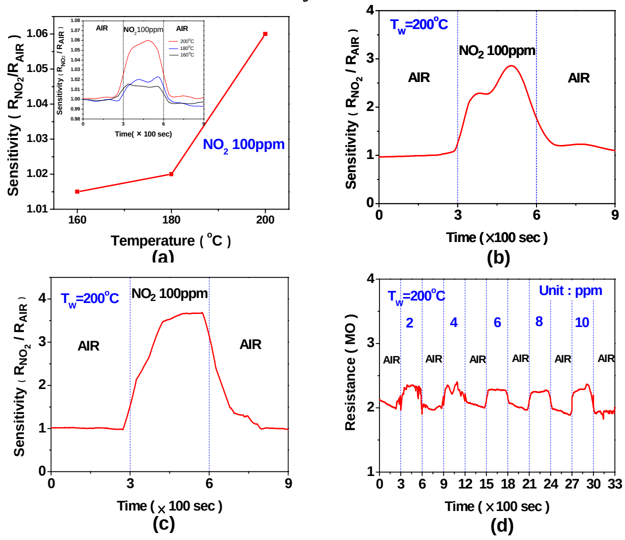

Fig.3 (a) Influence of the gas sensing performance on the working temperature of the gas sensor. Transient responsibilities of serially connected sensors to 100-ppm-NO_2 at 200^{o}C: (b) two sensors and (c) four sensors. (d) Sensing behavior of a four-serially-connected sensors to NO_2 of different contents.

4. Conclusions

In this study, a three-layer structure TONWs based gas sensor has been fabricated and their sensing performances to NO_2 at different working temperatures have been reported. Experimental results showed that the self-growth TOWNs were with a main phase of $W_{18}O_{49}$(010) and typical length and diameter of 0.1.5~0.4 μm and 17~25 nm, respectively. Good sensor performances with a sensitivity as high as 3.7 to NO_2 have been demonstrated by the proposed TONWs-based sensors because TONWs are with oxide vacancies and large SVR for gas absorption.

Acknowledgments

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