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H_2-Sensing Performance of 2D WO_3 Nanostructure—Effect of Anodization Parameter †

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Abstract: In this work, we investigate the effect of HNO_3 anodizing solution concentration ranging from 1.5 to 3 M on H_2-sensing performance of 2D WO_3 nanostructures prepared by anodizing sputtered tungsten films. The thickness of WO_3 nanosheets was found to reduce while the crystallinity degraded with increasing HNO_3 concentration. However, the nanosheets anodized in 2 M HNO_3 exhibited the highest response of 43.4 to 1 vol % H_2, which was one order of magnitude larger than those fabricated with other concentrations at the optimal operating temperature of 350 °C. In addition, the optimal nanostructures displayed good H_2 selectivity against NO_2, CH_4, C_2H_2 and C_2H_5OH.

Keywords: two-dimensional WO_3; semiconducting oxide; hydrogen sensor

1. Introduction

Two-dimensional (2D) nanostructures of metal oxides, particularly ultrathin nanosheets, have recently attracted substantial attention in gas-sensing applications due its large specific surface area, 2D-quantum effects and unique electronic properties [1–5]. Recently, 2D tungsten oxide (WO_3) nanosheets have been fabricated by a facile anodization method and demonstrated promising gas-sensing performance [5]. It is thus compelling to further optimize its performance by varying anodization parameters. In this work, 2D WO_3 nanostructures were prepared by anodization of sputtered tungsten (W) films with varying concentrations of HNO_3 anodizing solution and systematically characterized for gas-sensing towards hydrogen.

2. Materials and Methods

Firstly, 1 μm-thick W films were deposited on alumina substrates by radio-frequency (rf) sputtering in Ar at 2.6×10^{-3} Torr with an rf power of 100 W. The W films were then anodized in HNO_3 solutions with different concentrations ranging from 1.5 to 3.0 M at 60 °C. An anode voltage of 50 V was applied between the W film and Pt wire for 5 h. Next, Cr/Au intergitated electrodes were sputtered onto the WO_3 film on alumina substrates. Lastly, the sensors were annealed in air at 450 °C for 3 h. The annealed material was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Gas sensing tests have been carried out by the flow through method in a sealed stainless steel chamber with controlled temperature and humidity with the setup reported earlier [6]. Dry air certified bottles have been used as gas source and certified mass flow controllers to reproduce desired gaseous composition inside the test chamber. The sensors were tested toward hydrogen (H_2)

at 200–350 °C. Nitrogen dioxide (H_2), methane (CH_4), acetylene (C_2H_2) and ethanol (H_2) were also tested as possible interfering species.

3. Results and Discussion

3.1. Characterization Results

Typical morphology of anodized WO_3 films as shown in Figure 1 illustrates polygonal sheet structures having small thickness of below 50 nm. In addition, it was found that the thickness of nanosheets tended to reduce with increasing HNO_3 concentration. XRD patterns (Figure 2) confirm that the anodized films are nanocrystalline with reducing grain size and crystallinity as HNO_3 concentration increases.

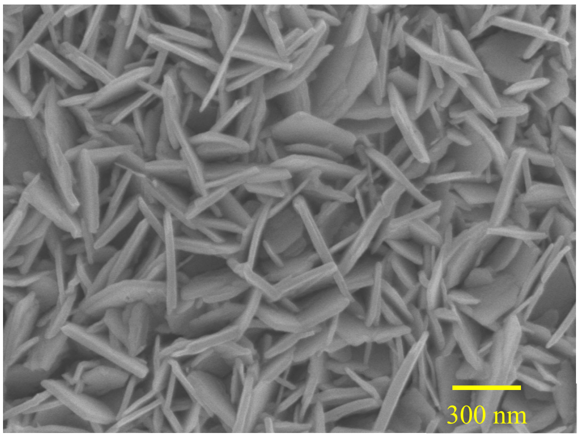

Figure 1. Typical SEM image of 2D WO_3 nano-structures prepared by anodization with 2 M HNO_3.

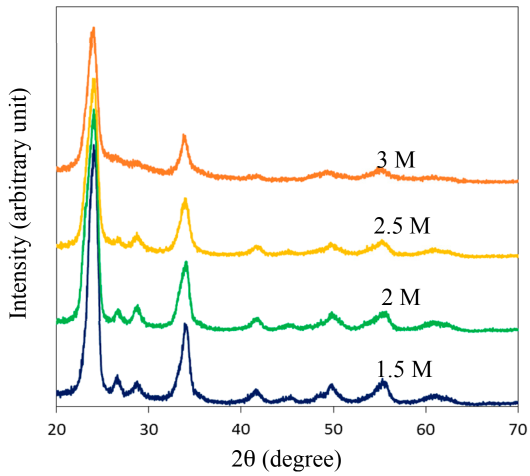

Figure 2. Typical XRD patterns of 2D WO_3 nanostructures prepared by anodization with different HNO_3 concentrations.

3.2. Gas-Sensing Results

Gas-sensing results towards various concentrations (0.015–1 vol %) of H_2 in Figure 3 showed that 2D WO_3 nanosheets exhibit typical n-type sensing behaviors with large resistance change at an optimal HNO_3 concentration of 2 M. The response variations as functions of concentration and temperature as demonstrated in Figures 4 and 5 shows that the 2D WO_3 nanosheets prepared in 2 M HNO_3 exhibited the highest response of 43.4 to 1 vol % H_2 at the optimal operating temperature of 350 °C, which was more than one order of magnitude larger than those anodized with other HNO_3 concentrations. Moreover, the optimal 2D WO_3 nanosheets displayed good H_2 selectivity against NO_2, CH_4, C_2H_2 and C_2H_5OH as displayed in Figure 6. The results might be ascribed to the moderate HNO_3 concentration that leads to optimally etched 2D WO_3 nanostructures with large surface area and good crystallinity.

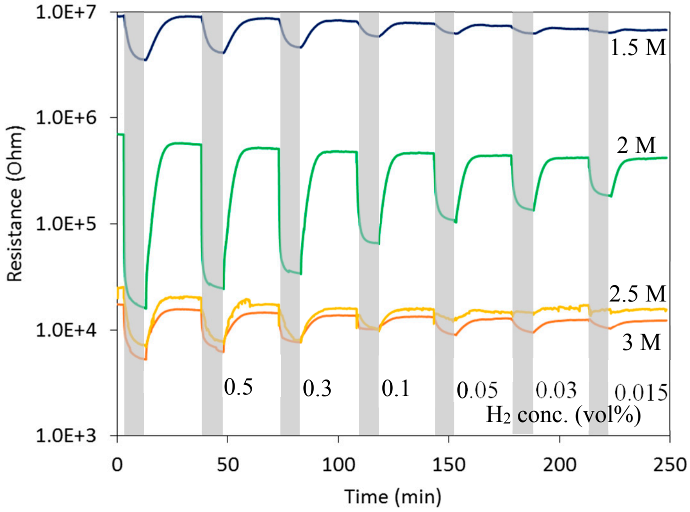

Figure 3. Resistance vs. time of 2D WO_3 nano-structures prepared by anodization with different HNO_3 concentrations subjected to various H_2 pulses at 350 °C.

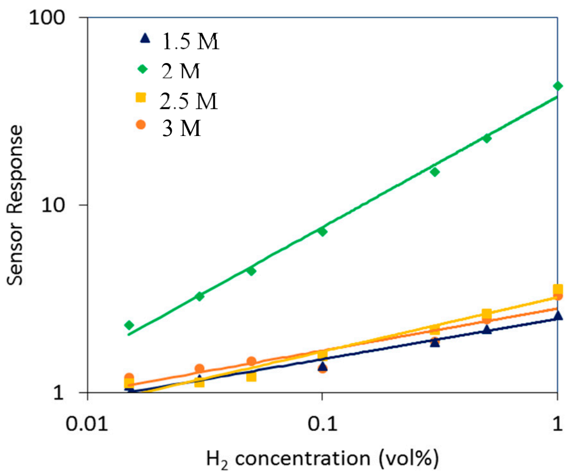

Figure 4. Response vs. H_2 concentration of 2D WO_3 nanostructures prepared by anodization with different HNO_3 concentrations at 350 °C.

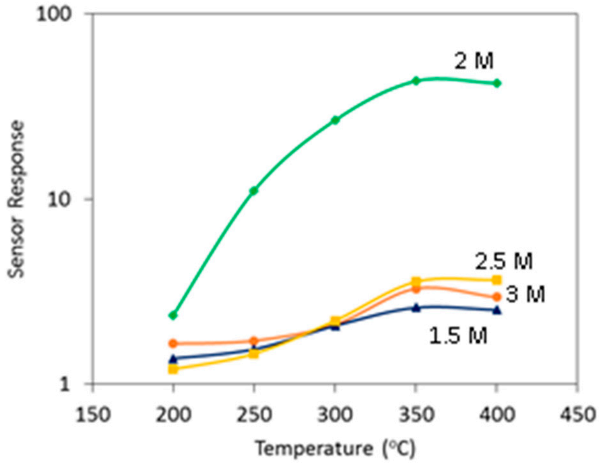

Figure 5. Response vs. operating temperature of 2D WO_3 nanostructures prepared by anodization with different HNO_3 concentrations at 1 vol % H_2.

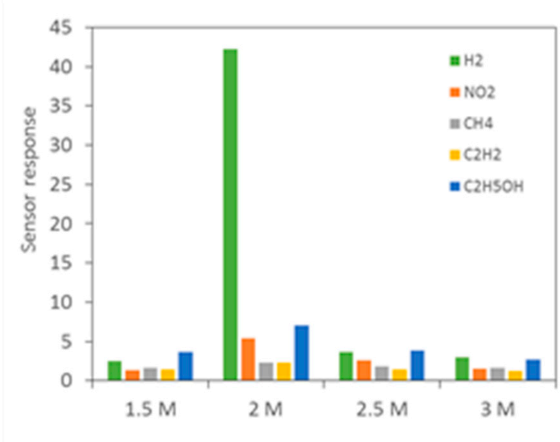

Figure 6. Selectivity histogram of 2D WO_3 nanostructures prepared by anodization with different HNO_3 concentrations at 1 vol %.

4. Conclusions

In conclusion, 2D WO_3 nanostructures prepared by anodizing sputtered tungsten films and the effect of HNO_3 anodizing solution concentration ranging from 1.5 to 3 M on H_2-sensing performance were systematically investigated. SEM and XRD analyses indicate that the thickness of WO_3 nanosheets tended to reduce while the crystallinity degraded with increasing HNO_3 concentration. However, the nanosheets anodized in 2 M HNO_3 exhibited the highest response of 43.4 to 1 vol % H_2, which was one order of magnitude larger than those fabricated with other concentrations at the optimal operating temperature of 350 °C. Moreover, the optimal nanostructures displayed good H_2 selectivity against NO_2, CH_4, C_2H_2 and C_2H_5OH.

Conflicts of Interest: The authors declare no conflict of interest

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