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Simple fabrication method of silicon/tungsten oxide nanowires heterojunction for NO_2 gas sensors

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ABSTRACT

Heterojunctions, formed at the interface between two different materials, have attracted much attention as a gas-sensing material. In particular, Si/tungsten oxide (WO_X) heterojunctions are well known to be capable of gas detection at low temperature and to increase the sensitivity to and selectivity of NO_2. However, during the fabrication process of the Si/WO_X nanostructure-based sensor it is difficult to control the synthesis position of the nanostructures; hence, it is complicated or time consuming. In this work, semiconducting gas sensors based on n-type silicon/n-type suspended tungsten oxide nanowire (WO_X NW) heterojunctions were fabricated by stress-induced method for WO_X NW synthesis on Si MEMS structures. With this fabrication technique, the growth position of the WO_X NWs can be controlled by patterning of the WO_X seed film, and the NWs can be synthesized by simply heating the seed film for 20 min. In addition, all fabrication processes consist of batch-processes. Unlike conventional WO_X-based sensors, the resistance of this sensor is reduced in the presence of NO_2, an oxidizing gas, due to the band bending phenomenon of the Si/WO_X NW heterojunction. The fabricated sensor can detect 500 ppb of NO_2 and exhibits excellent selectivity to CO and toluene, which are exhaust gases, like NO_2. This selectivity will be particularly useful when using sensors to detect NO_2 in exhaust gases of automobiles or factories.

1. Introduction

Nitrogen dioxide (NO_2), which is mainly emitted from automotive exhaust gas and industrial waste gas, is a typical air pollutant and causes acid rain and photochemical fog [1,2]. In addition, exposure to NO_2 is known to increase the risk of respiratory infections and pulmonary diseases such as emphysema and bronchitis [3]. Therefore, the development of gas sensors that can detect NO_2 rapidly and sensitively is very important. Various metal oxide-based gas sensors including tin oxide [4], tungsten oxide (WO_X) [5–9], zinc oxide [10], and indium oxide [11] have been extensively studied as sensing materials for detecting NO_2, and they are widely used because of their high sensitivity, small size, and low power consumption. However, such metal oxide-based sensors generally have poor selectivity between gases, which is one of the biggest obstacles in the commercialization of the sensors. Studies using a heterojunction with a combination of two substances as a gas sensing material have being conducted recently to overcome this disadvantage.

The interface between two materials or structures that have dissimilar electronic band structures forms a heterojunction. At the heterojunction, Fermi level equalization and band bending occur, which leads to charge transfer and the formation of a charge depletion layer. Many researchers reported recently that the sensitivity and selectivity of the semiconducting gas sensors can be improved by utilizing heterojunctions as sensing materials [12]. Among the various heterojunctions, Si/WO_X-based heterojunctions are known to selectively detect NO_2 at low temperature, and studies have been conducted to fabricate Si/WO_X heterojunction-based sensors through various methods [13–21]. Yan et al. fabricated porous Si (PS)/WO_X nanoparticle (NP) heterogeneous junctions by the dip coating method after preparing WO_X NP solutions through sol-gel synthesis [14]. This study has disadvantages in that the position of the WO_X NPs cannot be controlled and it takes more than 10 h to synthesize and integrate nanomaterials. Ma et al. synthesized WO_X nanowires (NWs) via a vapor-solid method to sublimate the tungsten powder in the furnace and condense it on the Si structure [16]. The method used in this study has the advantage of shortening the synthesis and integration time of nanomaterials to within 3 h; however, this method cannot control the integration position of the NWs. Wei et al. synthesized WO_X nanorods (NRs) on the Si structure via hydrothermal synthesis to fabricate a heterojunction [18].

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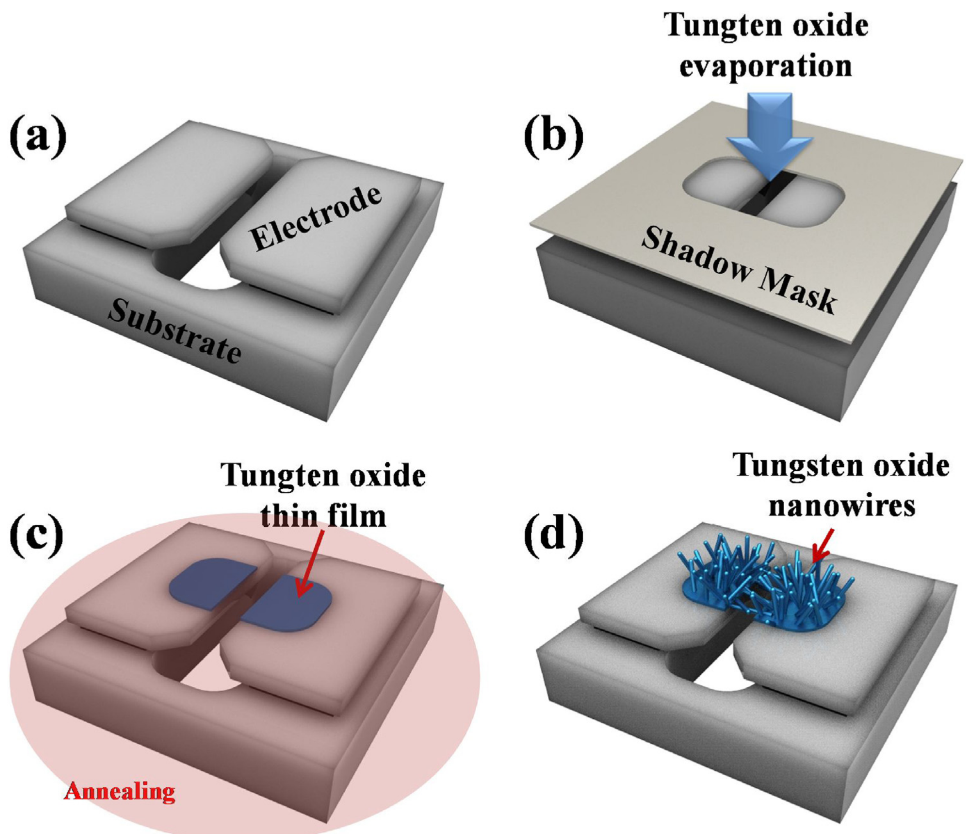

Fig. 1. Fabrication process of NO_2 sensors based on Si/WO_X NWs contact. (a) Fabrication of Si electrodes through MEMS process using a SOI wafer. (b) Evaporation of WO_X thin film through shadow mask for patterning. (c) Annealing the WO_X film in a furnace with 100 sccm of N_2 flow at 750 °C for 20 min. (d) Si electrodes connected by out-of-plane growth of NWs.

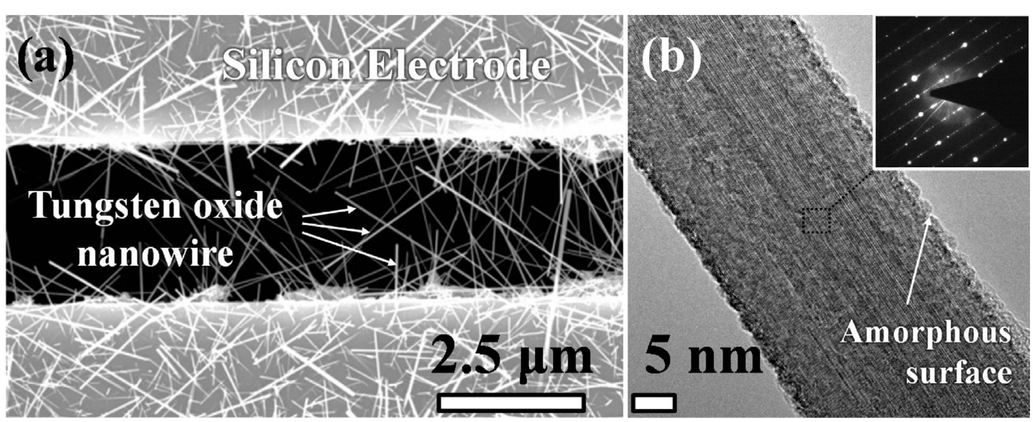

Fig. 2. (a) SEM image of WO_X NWs grown between two electrodes. (b) TEM image of a single crystalline WO_X NW. Inset image shows diffraction pattern.

In this study, it was possible to control the integration position of the nanomaterials by drop-casting the seed material; however, two steps and 4 h of heating are required for synthesis and integration. Recently, Yan et al. studied the fabrication of a Si/WO_X NW heterojunction structure by depositing a WO_X thin film on a PS structure and directly growing and integrating the NWs through two heating steps [21]. The synthesis and integration of nanomaterials used in this study took more than 4 h. Therefore, it is necessary to study the fabrication process that can be used to control the integration position of WO_X nanostructures and simultaneously achieve simplicity and rapidity.

In this study, we fabricated a semiconductor-type gas sensor based on n-type Si/n-type WO_X NW heterostructures via a stress-induced method of WO_X on Si structures. Unlike conventional vapor-solid [6–8], and solvothermal methods [9], the stress-induced method used in our research has the advantages of easy control of the synthesis position, absence of precursor, and simplicity of the process. The position of the NW can be adjusted through a shadow mask during the deposition of WO_X film, and the sensor fabrication can be completed through one step of a very short heating process (under 20 min), unlike in previous studies. In addition, the WO_X NWs are suspended between two facing Si structures, which improves the sensor sensitivity [22]. When exposed to NO_2, the fabricated sensor demonstrates a resistance change in the direction opposite to that of conventional WO_X-based sensors. We newly proposed the NO_2 sensing mechanism of the n-type Si/n-