Sensors and Actuators B 255 (2018) 1663–1670

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

An array of metal oxides nanoscale hetero *p-n* junctions toward designable and highly-selective gas sensors

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ARTICLE INFO

Article history:
Received 6 June 2017
Received in revised form 27 July 2017
Accepted 23 August 2017
Available online 5 September 2017

Keywords:
Metal oxide
Gas sensor
Nanoscale *p-n* junction
Electronic noses
Oblique-angle deposition

ABSTRACT

Nano-helical array of *p*-NiO/n-SnO_2 *p-n* junctions with well-defined and highly-gas-accessible hetero-interfaces is presented for designable and highly selective gas sensors. The gas sensor having the nanoscale *p-n* junction sensing layer with a top-and-bottom electrodes configuration was fabricated by conventional photolithography and oblique-angle deposition. The unique device structure enables a predominant modulation in barrier height at the hetero-interfaces, consistent with simulation results, resulting in unusual-yet-promising sensing behaviors upon H_2 and NO_2 exposure. Based on our experimental and simulation results, and the ability to fabricate a variety combination of metal oxides heterostructures with a reproducible and controllable way, we believe that it becomes possible to design and realize highly-selective sensor array electronic-noses optimized towards target gases on demand.

1. Introduction

Metal oxides gas sensors have been intensively studied due to their advantages of low cost, and simple fabrication and operation, thus widely used in many applications such as air quality monitoring, explosive gas detection, and healthcare [1–4]. However, conventional gas sensors with a single metal oxide layer detect the change of its bulk resistance upon gas exposure, thus show limited gas sensitivity and selectivity [1,5]. In this regard, metal oxides heterostructures, in which two different metal oxides form a physical interface, have recently become attractive candidates as sensing layers due to their potential to enhance gas sensitivity by a larger modulation in current through the heterojunction barrier than that through the bulk [6–8]. Furthermore, the degrees of freedom in the choice of independent materials and their various combinations are great for such heterostructures, which can improve the selectivity towards a target gas from mixture of various gases [6,9,10]. There have been numbers of attempts to fabricate metal oxides heterostructures as gas sensing layers [6–15], most of which are based on mixed composite[13] or particle-decorated structures [14,15] having randomly distributed heterojunctions. Although gas sensitivity and selectivity were reported to be enhanced, there have been remaining challenges such as poor stability and reproducibility in sensing performances and difficulty in quantitative investigation on gas sensing mechanism with such not-well-defined heterojunctions [6].

In order to take full advantages metal oxides heterostructures offer, fabrication and characterization of well-defined hetero-interfaces between metal oxides where current passes through with a diode-type characteristic are strongly required. One of simple ways to fabricate such heterostructures is stacking two different metal oxides thin films [16–20]. For example, conventional physical vapor deposition and photolithography were used for the formation of well-defined thin-film-based microscale heterojunctions [17,18] which, however, are not effective for obtaining a large current modulation due to a limited gas accessibility into the hetero-interfaces, calling for an array of nanoscale heterojunctions. Recently, air-bridge-structured nanowire heterojunction arrays with diode-type characteristics were reported [19]. However, the hetero-interfaces were small, randomly distributed, and formed with an uncontrollable way, which makes a systematic investigation of the effects of heterojunction on gas sensing properties difficult.

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http://dx.doi.org/10.1016/j.snb.2017.08.173
0925-4005/

Here, we demonstrated a nano-helical array of *p*-NiO/n-SnO_2 hetero *p*-*n* junctions as gas sensing layers where the heterojunctions are well-defined and gases can easily access to both metal oxides surfaces and hetero-interfaces. The nanoscale array, fabricated by oblique angle deposition (OAD) between top and bottom electrodes, shows *p*-*n* junction current-voltage (I–V) characteristics. Interestingly, the *p*-NiO/n-SnO_2 gas sensor shows a similar trend in current modulation under both reducing H_2 and oxidizing NO_2 gases, which is very unusual considering the changes of electrical properties occurring in the single *p*-NiO and the *n*-SnO_2 gas sensors. Such unexpected sensing properties can be explained by the predominant modulation in barrier height at the hetero-interfaces over the change in the carrier concentration of each oxide layer, which is confirmed by the Shockley diode equation as well as the simulation results obtained by Sentaurus TCAD software. Our experimental and simulation results, together with the ability to fabricate a variety combination of metal oxides heterostructures by using reproducible and controllable OAD, can give a promising strategy to design and realize highly-selective sensor array electronic-noses optimized towards target gases on demand.

2. Methods

2.1. Fabrication of the NiO nanohelixes (NHs) sensor, SnO_2 NHs sensor, and NiO/SnO_2 NHs sensor

Gas sensors with three sensing layers (*p*-NiO NHs, *n*-SnO_2 NHs, *p*-NiO/n-SnO_2 NHs) are composed of the bottom electrode, array of NHs sensing layer, the top electrode, and the pad electrode, and were fabricated by using conventional microelectronics fabrication processes including photolithography and physical vapor deposition. At first, a Ti/Pt (5 nm/20 nm) bottom electrode was deposited on a SiO_2/Si substrate by electron beam (e-beam) evaporation, for all three devices. Then, arrays of NHs layer were formed by OAD. For the single *p*-NiO NHs sensor, a 230-nm-thick NiO NHs was deposited with the vapor flux angle of 80°, the deposition rate of 1.5 Å/s and the substrate rotation speed of 0.1 rpm on the bottom electrode. Then, the Pt electrode was deposited with the thickness of 180 nm on the *p*-NiO NHs layer. For the *n*-SnO_2 NHs device, a 450-nm-thick SnO_2 NHs was deposited with the condition of 80°, 2.2 Å/s, and 0.1 rpm, followed by the deposition of Ti/Au (20 nm/150 nm) for ohmic contact formation. For the *p*-NiO/n-SnO_2 NHs heterojunction sensor, a 180-nm-thick NiO NHs and a 250-nm-thick SnO_2 NHs were deposited in order with the same condition as each single NHs layer, and a Ti/Au (20 nm/150 nm) top electrode was deposited. Here, all the samples were annealed at 500 °C for 30 min in air ambient right after the NHs deposition, and at 300 °C for 5 h in air ambient after top electrode deposition. Top electrodes were formed by OAD with a vapor flux of 45° to prevent penetration of the metal through the highly-porous NHs layer. Finally, a Ti/Au (20 nm/200 nm) pad electrode was deposited on both the top and bottom electrodes for all the devices.

2.2. Gas sensing measurement

Gas sensing properties of the devices were measured in the chamber probe station equipped with an electrical measurement system, a temperature-control system, and a precisely-controlled gas flow system. The I–V characteristics were measured by probing the two pads of the device shown in **Fig. S1**, and applying electrical biases to bottom electrode with grounded top electrode. The measurement temperature was controlled to be 200 °C, which was optimized temperature for the large gas response. Before gas exposure, pure dry air (O_2/N_2) was introduced in the chamber under 1 atm. For H_2 and NO_2 gas sensing measurements, H_2 pulses with 500 ppm and NO_2 pulses with 20 ppm concentrations balanced by dry air were introduced to the chamber, respectively. Electrical properties after gas exposure were stabilized within 10 min, and I–V curves were obtained from the stabilized states. The I–V curves were recovered to the initial ones after stopping H_2 or NO_2 exposure and dry air introduction. The I–V responses were measured with the voltage sweep step of 0.05 V from −3 V to 3 V.

2.3. Simulation methods

All the single and heterojunction NHs were simulated using Sentaurus TCAD software. Simple drift-diffusion transport equations were coupled with Poisson and carrier continuity equations self-consistently. Fermi-Dirac statistics were adopted as well Shockley-Read-Hall and Auger recombination models. Schottky contact at the metal oxide/metal interfaces was also considered for the exact calibration with I–V data. Temperature in the simulation platform is fixed at 200 °C, which is the same under gas sensing measurement condition.

The intrinsic properties of metal oxide are also included in the simulation platform. Electron affinity, bandgap, constant electron and hole mobilities, dielectric constants, and effective density-of-states (DOS) of NiO and SnO_2 are obtained from the previous studies as shown in **Table S1**. The NiO and SnO_2 have Ni vacancies (V_{Ni}) and Sn vacancies (V_{Sn}), respectively, and O vacancies (V_O) in common, depending on the fabrication methods and conditions. It is known that V_{Ni} forms acceptor-like states, while V_O forms donor-like states in the NiO. For all the experimental and simulated studies, the NiO has larger number of V_{Ni} located above the valence band (E_V), capturing electrons below E_V, thus forming a *p*-type semiconductor [21–23]. On the other hand, the SnO_2 has a large number of V_O located below the conduction band (E_C), donating electrons above E_C, thus forming an *n*-type semiconductor [24,25].

These vacancies are equivalently modeled as defect states inside the metal oxide, which generate free electrons or holes depending on the kinds of the defect states. Each metal oxide has effective, single-level defect states. By calibrating the energy level and concentration of the defect states along with the metal work function for the electrodes, the simulated I–V data were fitted well to the measured data. The difference of Pt work function for the NiO and SnO_2 NHs could be caused by different interface materials and process condition (**Table S1**). The dipole layer at the Pt/SnO_2 contact under H_2 exposure is simply modeled as the change of Pt work function. The adsorbed oxygens are modeled as the fixed charges at the surface of metal oxides and worked as the variables only for the detection of different gas.

3. Results and discussion

The gas sensors having an array of *p*-NiO/n-SnO_2 nanoscale hetero *p*-*n* junctions were fabricated by using conventional microelectronics fabrication processes including photolithography and physical vapor deposition. The schematic drawings of the device is shown in Fig. 1a, and the optical microscopy image of the fabricated device is shown in **Fig. S1**. An array of nano-helical metal oxides *p*-*n* junctions was formed by OAD. At the initial stage of OAD, highly-oblique vapor flux makes the nuclei of the depositing material and shadow region behind them where subsequent vapor flux cannot reach. By controlling oblique angle, deposition rate, and substrate rotation speed, arrays of various three-dimensional nanostructures with any evaporable metal oxides can be fabricated in a simple, reproducible, and cost-effective way [11,26,27]. Here, *p*-type NiO NHs were deposited on the Ti/Pt bottom electrode, followed by the deposition of *n*-type SnO_2 NHs forming nanoscale hetero *p*-*n* junctions. Then, Ti/Au top and pad electrodes were deposited. The