Metal Oxide Nanocolumns for Extremely Sensitive Gas Sensors

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Abstract

Highly ordered SnO$_2$ and NiO nanocolumns have been successfully achieved by glancing-angle deposition (GLAD) using an electron beam evaporator. Nanocolumnar SnO$_2$ and NiO sensors exhibited high performance owing to the porous nanostructural effect with the formation of a double Schottky junction and high surface-to-volume ratios. When all gas sensors were exposed to various gases such as C$_2$H$_5$OH, C$_6$H$_6$, and CH$_3$COCH$_3$, the response of the highly ordered SnO$_2$ nanocolumn were over 50 times higher than that of the SnO$_2$ thin film. This work will bring broad interest and create a strong impact in many different fields owing to its particularly simple and reliable fabrication process.

Keywords: Gas sensors, Oxide semiconductors, SnO$_2$, NiO, Glancing angle deposition

1. INTRODUCTION

Over the past decade, rapid developments in nanoscience and nanotechnology have accelerated research in nanomaterials [1]. Generally, nanomaterials can be classified as having three different morphologies or nanostructures (1D, 2D, or 3D), which affect the electrical properties of nanomaterials based on metal oxide [2]. In particular, 1D nanostructures based on metal oxide are more applicable to nanoelectronics and nanodevices. The widths and lengths of 1D nanostructures are confined to the nanoscale range between 1 and 100 nm, but the lengths can be several micrometer or more, leading to anisotropic nanostructures with high surface-to-volume ratios [3-6].

Thus, various one dimensional (1D) nanostructures such as nanorods, nanowires, nanoneedles, nanofibers, and nanobelts based on metal oxide have been extensively studied, and their unique and fascinating properties have already been demonstrated by applying them as gas sensors, biosensors, smart windows, solar cells, supercapacitors, photodetectors, light-emitting diodes, and field emissions [7]. However, most 1D nanostructures have been fabricated using a solution-based approach or by vapor-liquid-solid growth [8]. Such methods are not suitable for practical devices since they causes poor reliability and reproducible electrical properties owing to nonuniform connections between randomly distributed individual nanostructures [9]. Further, integrating them with low-cost and high-yield mass production processes remains a challenge [10].

Recently, a glancing-angle deposition (GLAD) technique based on the physical vapor deposition (PVD) process has emerged as a promising method, that is cost effective and can uniformly fabricate a variety of well-ordered nanostructures, (i.e., aligned 1D nanostructures such as nanorods, nanoblades, and zigzag nanocolumns) by controlling the incident angle and optional substrate rotation [11,12].

Chemiresistive gas sensors have a profound influence in the areas of medical diagnosis, food processing, military environments, personal safety, public security, agriculture, and the automotive and aerospace industries [13-17]. One of the most promising advantages of chemiresistive gas sensors is the implementation of simple, cost-effective, power-efficient, reliable, sensitive, and selective nanodevices for real-time analysis chemical analytes [18]. In this respect, semiconductor gas sensors based on metal oxides have been investigated owing to various
advantages, including simple operation, cost competitiveness, and ability to detect a large number of gases compared with other gas sensors such as optical sensors and electrochemical sensors [19, 20]. Generally, it is well known that semiconductor gas sensors based on metal oxide are affected by three main factors for high sensor performance: transducer function, utility factor, and receptor [21]. Based on these main factors, various attempts with large surface-area-to-volume ratios have been conducted to achieve high sensor performance. However, these nanostructured metal oxides do not exhibit the impressive results owing to aforementioned problems such as poor stability and nonuniformity of the nanostructures [9].

In this paper, we present a simple technical process for an extremely sensitive gas sensor based on well-ordered 1D nanostructures. Highly ordered SnO$_2$ and NiO nanocolumns have been successfully created by GLAD using an electron beam evaporator. We create our gas sensor based on highly ordered SnO$_2$ and NiO nanocolumns, and use the sensor to investigate gas sensing properties. When all gas sensors are exposed to various gases such as C$_2$H$_5$OH, C$_6$H$_6$, and CH$_3$COCH$_3$, the response of a highly ordered SnO$_2$ nanocolumn is more than 50 times higher that of SnO$_2$ thin film. This can be attributed to the formation of a double Schottky junction between the SnO$_2$ nanocolumns.

2. EXPERIMENTAL

2.1 Fabrication

Pt/Ti (150 nm/30 nm thick) interdigitated electrodes (IDEs) were fabricated on a SiO$_2$/Si substrate (1 µm/550 µm thick) using photolithography (lift-off procedure). The distances between the Pt/Ti IDEs and the sensing area were approximately 5 µm and 1 mm × 1 mm respectively. Before depositing the sensing films, Pt/Ti IDE patterned SiO$_2$/Si substrates were cleaned in acetone and ethanol followed by drying in nitrogen gas. To make SnO$_2$ and NiO thin film, RF magnetron sputtering was utilized. The base pressure, working pressure, RF power and gas flow rate were 2 10$^{-6}$ mTorr, 10 mTorr, 50 W and 30 sccm, respectively. To synthesize SnO$_2$ and NiO nanocolumns, evaporation using an electron beam evaporator was carried out at a glancing angle. The substrate was located 30 cm away from the crucible, tilted at 81º. The base pressure and growth rate were 5 10$^{-6}$ mTorr and 1 Å s$^{-1}$, respectively. All fabricated specimens were annealed at 550 ºC for 2 h in ambient air.

2.2 Characterization

X-ray diffraction (XRD) was used to analyze films using an X-ray diffractometer (DMax2500). The morphology of the fabricated SnO$_2$, NiO nanocolumns was observed by a field emission scanning electron microscope (FESEM) using an acceleration voltage of 15 kV and a working distance of 10 mm.

2.3 Sensor Measurements

Gas sensing properties of the SnO$_2$ thin film, SnO$_2$ nanocolumn, NiO thin film and NiO nanocolumn were measured in a quartz tube with external heating. The flow gas was changed from dry air to a calibrated target gas (balanced with dry air). A constant flow rate of 500 sccm was used for the dry air and target gas. The response of the samples was accurately determined by measuring the baseline resistance in dry air and the fully saturated resistance after exposure to the target gas. The resistances were measured at a DC bias voltage of 0.1 V using a source measurement unit (Keithley 236). The gas flow was controlled using mass flow controllers and all measurements were recorded on a computer using LabVIEW over a General Purpose Interface Bus (GPIB) interface.

3. RESULTS AND DISCUSSIONS

3.1 Crystal Structure and Microstructure

Fig. 1 shows a schematic diagram of the fabrication procedure of well-ordered SnO$_2$ and NiO nanocolumns using electron beam
Young Geun Song, Young-Seok Shim, Soo Deok Han, Hae Ryong Lee, Byeong-Kwon Ju, and Chong Yun Kang


The density and length of the 1D nanostructures fabricated by GLAD are closely related to the electrical properties with accessibility of target gases. Our previous research showed that metal oxide nanocolumns deposited at 80° were optimal for gas sensing [9]. The final structures were observed with a scanning electron microscope (SEM), as shown in Fig. 2. Although all samples were deposited with the same thickness and condition at 80°, the length and diameter of each samples is different. These results are attributed to the initial nucleation rate and size of the material. The diameter of the well-ordered SnO$_2$ and NiO are approximately 50 nm and 30 nm, respectively. It is clear that the SnO$_2$ forms larger nucleated islands than NiO.

The crystallinity of well-ordered SnO$_2$ and NiO annealed at 550°C for 2 h were charact erized by XRD measurement. As shown in Fig. 3, all diffraction peaks of the two samples can be indexed by SnO$_2$ (JCPDS no. 41-1445) and NiO (JCPDS no. 47-1049). No other impurity phases were detected by the XRD, except for silicon wafer peak of NiO nanocolumn at 53°. The as-deposited film crystallized very well during the annealing processes.

### 3.2 Gas-Sensing Properties

In order to measure their gas-sensing properties, well-ordered SnO$_2$ and NiO were deposited on SiO$_2$/Si substrates with Pt IDEs. For comparison, SnO$_2$ and NiO thin films were also measured. Upon exposure to ambient air, the resistance of both the SnO$_2$ thin film and nanocolumns increased, however, the base resistances were different. The SnO$_2$ nanocolumns exhibited a higher resistance than SnO$_2$ thin films owing to the formation of a double-Schottky barrier between the nanocolumns. The response of the well-ordered SnO$_2$ nanocolumns to 50-ppm C$_2$H$_5$OH, C$_6$H$_6$, and CH$_3$COCH$_3$ was measured at a working temperature of 300°C, as shown in Fig. 4 (a–c).

The resistance decreased abruptly upon exposure to C$_2$H$_5$OH, C$_6$H$_6$, and CH$_3$COCH$_3$, which is typical behavior for an n-type semiconductor gas sensor. By contrary, the base resistance for NiO thin film and nanocolumns increases in ambient air. When the NiO samples were exposed to 50-ppm C$_2$H$_5$OH, C$_6$H$_6$, and CH$_3$COCH$_3$, the resistances of the NiO and NiO nanocolumns increased. This was consistent with the behavior of p-type semiconductor gas sensors, as shown in Fig 4 (d–f). In order to identify enhancements to the gas-sensing properties, the gas sensitivity was calculated and defined as $R_{gas}/R_{air}$ for n-type sensors and $R_{air}/R_{gas}$ for p-type sensors, $R_{gas}$ is the resistance of the film in a test gas, and $R_{air}$ is its resistance in dry air for each samples.

The well-ordered SnO$_2$ and NiO nanocolumns exhibited substantially higher sensitivities than those of thin films. In particular, the sensitivities of well-ordered SnO$_2$ nanocolumns were enhanced by approximately several tenth of the scales because of large surface-to-volume ratios, porous structures, small grain sizes, and enlarged depletion regions in the grain.

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**Fig. 2.** Plain-view SEM micrographs of (a, b) SnO$_2$ and NiO. (c, d) show cross-sections of (a, b).

**Fig. 3.** XRD analysis of (a) SnO$_2$ thin film and nanocolumns. (b) NiO thin film and nanocolumns.
3.3 Gas-Sensing Mechanism of n- and p-Type Materials

Although both n- and p-type metal oxides establish electrical core-shell layers by absorbing oxygen at the surface area, they exhibit significantly different sensing mechanisms. In n-type materials (Fig. 5a), resistive shell-to-shell contacts are formed between the grains in metal oxides. Therefore, equivalent circuits of n-type gas sensors can be demonstrated as serial connections between semiconducting cores and resistive interparticle contacts. By contrast, the sensing mechanisms in p-type materials can be demonstrated by competition between parallel paths, resistive cores and p-semiconducting shell regions (Fig. 5b). In addition, Fig. 5c shows the scheme of double Schottky barrier model established by interparticle contacts. Double Schottky barrier is related with shell-to-shell contacts which are resistive shell in n-type and p-semiconducting (hole accumulated regions) shell in p-type. In this respect, the p-semiconducting (conductive) shell have lower double Schottky barrier than n-type. This is compensated with other nanostructure effects, porous morphology, small grain size, large surface-to-volume ratios and so on. Hence, a 1D nanocolumn is more suitable to n-type than p-type materials.

4. CONCLUSIONS

We reported that porous nanocolumns were synthesized by the GLAD method. For application in gas sensors, well-ordered SnO$_2$ and NiO nanocolumns are fabricated on Pt IDEs-patterned SiO$_2$/Si substrates. Upon exposure to various gases, all nanocolumns exhibited higher responses than those of thin films. Most
importantly, the increasing ratio of the sensitivity of SnO$_2$ are higher than that of the NiO nanocolumns owing to different gas sensing mechanism. As a results, it indicated that the n-type material was more enhanced than the p-type with regard to ethanol, acetone, and benzene gases.

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