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Synthesis of self-bridged ZnO nanowires and their humidity sensing properties

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ABSTRACT

In this study, self-bridged ZnO nanowires were grown by a simple annealing process and their humidity sensing properties were investigated. The wurzite structure and high crystallinity of the ZnO nanowires were confirmed by XRD and PL analyses. The humidity sensing characteristics varied exponentially with increasing humidity. A conventional sensor device should have good repeatability and superior humidity sensing response. The experimentally obtained response and recovery times of the ZnO nanowires were 35.3 and 32.6 s, respectively. A possible humidity sensing mechanism is also proposed.

1. Introduction

Sensors are common devices employed to detect various physical parameters in different environments. The use of sensors has dramatically increased due to their convenience. Detecting explosive gas or biohazardous chemicals can save people and prevent disasters. Also, specific sensors are utilized in the fields of iris or fingerprint recognition for private security.

Humidity is an important historical factor in natural environments related to human life. Humidity affects agriculture, the preservation of historic relics, food science, human science, and meteorology, among other fields. Therefore, accurate measurement of the humidity is of significant interest in various research fields. For the development of humidity sensors, many materials, including carbon group materials such as CNTs [1,2] and graphene [3,4], metal oxides, conducting polymers [5], and ceramic compounds [6–8], have been utilized. Among them, metal oxides such as TiO_2 [9,10], ZnO [11], SnO_2 [12], Al_2O_3 [13], and CuO [14,15] have attracted considerable attention for the implementation of humidity sensors because of their superior sensing properties, simple fabrication, low cost, and clear operating mechanism. In particular, ZnO, which has a direct wide band gap (3.4 eV) with a hexagonal wurzite structure, is a promising humidity sensing material. However, many researchers reported that ZnO-based film type sensors have limitations related to their sensing properties. In order to overcome constraints, one-dimensional (1D) nanostructures of ZnO including nanowires [16], nanotubes [17], nanorods [18], nanobelts [19], nanofeathers [20], and nanosheets [21] are used because of their high surface to volume ratio and uniquely anisotropic structures.

For 1D nanostructures, vapor-liquid-solid (VLS) and vapor-solid (VS) techniques have been used for the growth of ZnO nanowires [22,23]. The synthesized nanowires are rearranged perpendicular to the substrate using a “pick and place” technique. However, this approach requires a lot of time and effort. Although enormous efforts have been made for the mass formation of ZnO nanowires, its directional growth between microelectrodes for nano-device fabrication remains full of challenges.

In this study, self-bridged ZnO nanowires were synthesized by a simple annealing process and used as a humidity sensor material. The surface morphology and crystal structures were investigated by SEM and XRD. The humidity sensing characteristics were verified using a Keithley 2636A under various conditions. In the next chapter, the method employed to fabricate the ZnO wires and the

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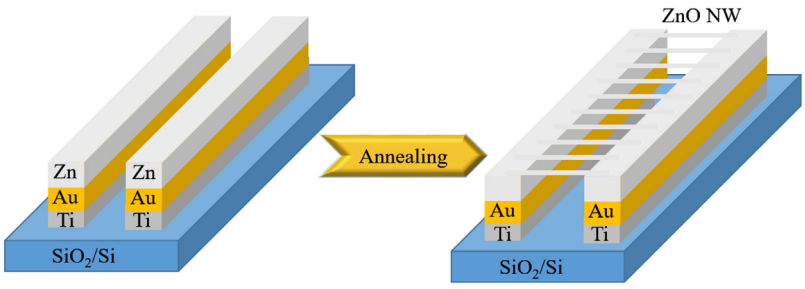

Fig. 1. Scheme of the ZnO nanowire growth process through annealing.

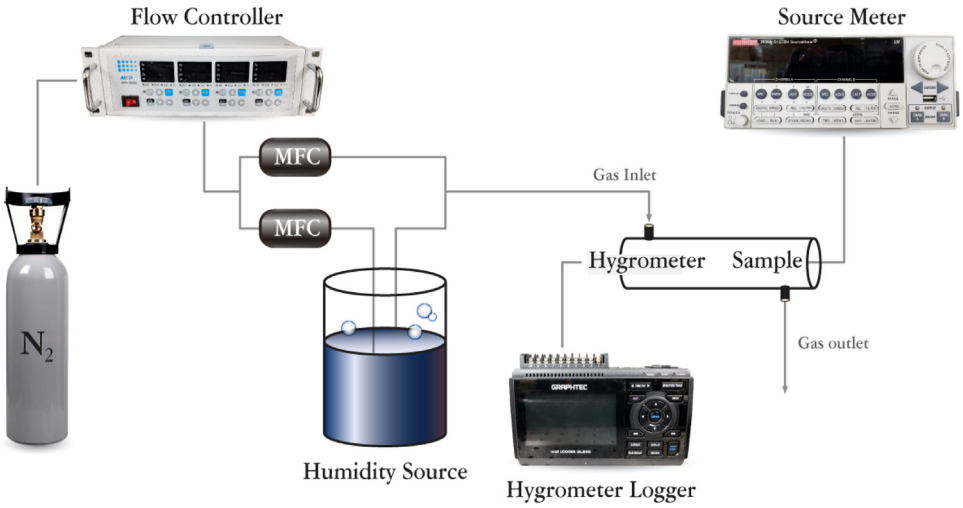

Fig. 2. Scheme of the experimental self-developed humidity sensing environment.

humidity sensing mechanism of ZnO are discussed while the relative humidity (RH) was varied (1.74–61.28%) at room temperature.

2. Experimental

2.1. Preparation of ZnO NWs

A patterned micro electrode was used for the substrate which consisted of a Au/Ti coating on a SiO_2 wafer prepared by a conventional photo-lithography patterning process. Au and Ti with thicknesses of 200 nm and 20 nm, respectively, were deposited on a SiO_2 wafer using an E-beam evaporator. The distance and the length of the two Au/Ti electrode was 2 μm and 100 μm, respectively. An electrochemical deposition method was used for the deposition of Zn on the Au electrodes. A Pt-coated plate and Ag/AgCl electrodes (0.197 V vs. SHE) were utilized as the anode and reference electrode, respectively. Electrochemical deposition was performed using a choronoamperometry method with a potentiostat (AMETEK VersaStat3). The electrolytes contained 0.1 M $ZnCl_2$ and 1 M KCl as the zinc ion source and supporting electrolyte, respectively [24]. A voltage of −1.1 V (vs. a Ag/AgCl electrode) was applied to a micro electrode for 35 s at 25 °C. The pH of the electrolytes was adjusted to 2.5 by adding 10% HCl. After the deposition process, ZnO nanowires were grown in a tube furnace under dry gas conditions at 600 °C for 4 h. The samples were placed in the middle of the furnace. Dry gas consisting of 21% O_2 and 79% N_2 was fed into the tube furnace. The flow rate was maintained at 1 L/min using a mass flow controller. After the annealing process, nanowires were randomly grown on the gold electrode. The ZnO nanowire growth process is represented schematically in Fig. 1.

2.2. Characterization of synthesized ZnO nanowires

The surface morphology of the ZnO nanowires was evaluated using a field emission scanning electron microscope (FE-SEM, MIRA3, Tescan Co.). The microstructure of the ZnO nanowires was characterized by X-ray diffraction (XRD, Rigaku D, MAX-2500). Also, the photoluminescence spectrum (PL, Nano Log® spectrofluorometer, Horiba Scientific) was measured to evaluate the quality of the ZnO nanowires with excitation at 325 nm. The electrical properties were measured using a 2-point probe station in the range from −1 V to 1 V using a semiconductor analyzer (4145B semiconductor parameter analyzer, HP).

2.3. Humidity measurement

Fig. 2 shows the humidity measuring system which was developed to verify the humidity sensing properties of the ZnO NWs. The system consisted of a mass flow controller, a quartz chamber, a hygrometer, and a humidity source. The humidity was controlled by changing the ratio of dry gas to wet gas. The wet gas was made by using a humidity source (Duran SL. BOT2084) with dry gas. The prepared sensors were put in a quartz chamber and the variation of resistance was recorded using an electrical source meter (Keithley 2636A). The humidity was varied from 1.73 to 82.13%. Initially, the chamber was maintained at the lowest humidity. When the sensing signal reached steady state, the humidity was quickly changed by adjusting the ratio of dry gas to wet gas. The sensitivity is represented by R_{Dry}/R_{RH}, where R_{RH} is the resistance with the varied humidity and R_{Dry} is the resistance with the lowest humidity. The response and the recovery time are defined as the time to achieve 90% of the total resistance variation. The ZnO NWs humidity sensors