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Pyramid-Shaped ZnO Particles with High Sensitivity to Ethanol Gas

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Abstract:
We report the fabrication of ZnO pyramid-shaped particles with remarkably high sensitivity to ethanol gas. The ZnO pyramid-shaped particles were synthesized solvothermally under agitation in ethylene glycol and water solvent. The agitation resulted in dispersion of the pyramid-shaped particles rather than spherical aggregates. TEM studies revealed that the base of the pyramid-shaped particles is the (0001) plane and the six side surfaces are the {10-1-1} plane. Gas sensing response was evaluated as the ratio of electrical resistance of the ZnO particulate layer in air to that in ethanol. The highest gas sensing response value to 50 ppm ethanol gas was about 10000, which is remarkably higher than that of previously reported ZnO particles. The influence of the crystal facets and the polarity is discussed.

Key words: Zinc oxide, ethanol gas sensor, crystal facets, metal oxide semiconductor, solvothermal process

Introduction

Highly sensitive and reliable gas sensors are useful for monitoring of air quality, detection of flammable or toxic gases and medical diagnosis. The gas sensors using metal-oxide semiconductor have advantages including simple structure, low cost, rapid response and high sensitivity. Their gas detection is based on the reversible change in the electrical conductivity of the metal oxide induced by gas-surface interactions.

Zinc oxide (ZnO) is an n-type semiconductor and one of the metal-oxide-semiconductor materials for gas sensors. It is also widely used in electronic applications, such as varistors, transparent electrodes, surface acoustic wave filters and phosphors. Control of the morphology of ZnO nanostructures has been intensively investigated and a wide variety of morphologies have been observed for particles and thin films. Various ZnO nanostructures have been studied for gas sensor applications.

To improve the gas sensors performance, the design and control of the particle size, porosity and the catalyst additives have been studied. Furthermore, the particle shape and the crystal facets have attracted interest due to their effect on the gas sensing properties. Past studies showed that the (0001) plane was the most efficient surface for ethanol gas sensing by ZnO, because ethanol molecules are well adsorbed on the (0001) surface. Although high sensing properties on higher surface energy facets have been expected, successful results have not yet been obtained.

In this study, we report a remarkably sensitive ethanol sensor using pyramid-shaped ZnO particles. The influence of the morphology on the ethanol gas sensing properties is discussed.

Experimental procedure

Zinc acetate anhydride and hexamethylenetetramine (HMT) were dissolved separately in solvent of 87.5 vol% EG and 12.5 vol% water. The two solutions were mixed and placed in Teflon-lined stainless steel cylindrical chambers and were then heated at 90°C for 3 h using a heating oven with stirrer. When aqueous HMT solutions are heated, the HMT decomposes to formaldehyde and ammonia, which acts as a base and induces ZnO precipitation. The resultant precipitates were separated by centrifugation, washed with ethanol via ultrasonication three times and dried at room temperature.

For the sensor device, the ZnO powder was dispersed in EG and the slurry was drop-deposited on a gold interdigital electrode with a 100 μm pitch sputtered on a silica glass

substrate and dried. Au wire electrodes were attached to the device using Au paste and then the device was heated in air at 400°C.

The electrical resistance was measured under gas flow at 100 sccm of synthetic air and 1–50 ppm ethanol gas. The size of the chamber was about 500 cm^3. The device was heated with an external furnace. The sensor response, S, was defined as $S = R_a/R_g$, where R_a and R_g are the sample resistance in the synthetic air and ethanol gas, respectively. For flushing the adsorbed gas from the particles, the samples were annealed in air at 400°C for 3 h after each experiment.

Results

Without agitation during solvothermal process, spherical particles of about 2 μm were precipitated (Fig. 1). The particles were composed of small pyramid-shaped crystallites [1, 2]. When the solvothermal procedure was carried out under agitation, dispersed ZnO particles were precipitated instead of spheres. The obtained particles were about 20 nm and have pyramidal shape with (0001) on the bottom and {10-1-1} on the side surfaces (Fig. 2). ZnO has a wurtzite-type crystal structure and shows spontaneous electrical polarization along its c-axis. There are two types of ZnO pyramid particles with opposite polarity.

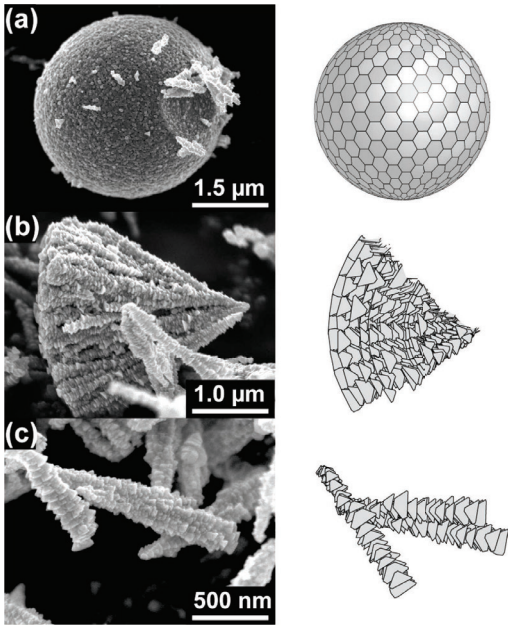

Fig. 1. SEM photographs and the corresponding illustrations of (a) spherical particle, (b) circular cones and (c) wedge-shaped fragments [1].

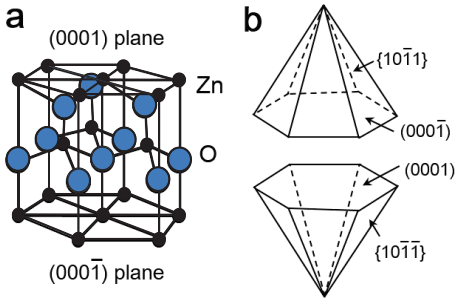

Fig. 2. Schematics of (a) ZnO wurtzite crystal structure and (b) two pyramids with opposite polarity.

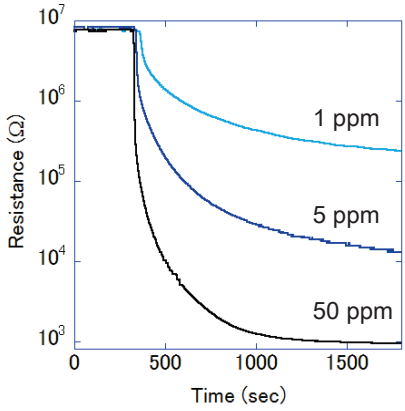

Fig. 3. Dynamic response of pyramid shaped ZnO particles to ethanol gas in air at 320ºC [3].

The pyramid particles showed an extremely high sensor response to ethanol gas [3]. Figure 3 shows the dynamic response to ethanol gas in air (1, 5, and 50 ppm) measured at 320ºC. The response value was about 10000 to 50-ppm ethanol gas, which was much higher than the previous best ZnO nano particles [4] and ZnO pyramid particles with opposite polarity [5]. The unique features of the present ZnO particles, i.e. the pyramidal shape and the crystal planes, most likely brought about the exceptionally high gas sensing properties as well as pore structure for the pyramidal shaped ZnO particles.

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