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A simple and cheap way to produce porous ZnO ribbons and their photovoltaic response

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Abstract

A simple and cheap method is proposed to achieve porous ZnO ribbons by oxidation of ZnS ribbons in the air. ZnS has a fully transformation to ZnO at an annealing temperature of 700°C from energy dispersive X-ray spectra and X-ray diffraction patterns. Scanning electron microscopy images indicate that ZnO ribbons keep the original shapes of ZnS, but produce some ordered and uniform pores on their surfaces. The photovoltage spectrum of ZnO/N3 indicates such dye-porous ZnO ribbons may be used in the dye-sensitized solar cells. The porous ZnO ribbons may also find potential applications in catalyst, sensor, and molecular selection. This technique to produce porous ribbons may also be applied to prepare other porous metal oxide ribbons.

Keywords: Semiconductors; Porosity

1. Introduction

Nowadays, lots of effort has been put into the fabrication of one-dimensional (1D) nanostructures for their wide applications in the field of optical, electronic, magnetic, sensor, etc. [1–4]. Among them, ZnO has attracted quite a large amount of attention for its unique properties and 1D structure. Control of spatial variation along or within 1D nanostructures may impact their properties. For example, gas sensor using porous structure, which has a very high surface-to-volume ratio, has a higher sensibility than that based on single-crystalline materials [5,6]. Furthermore, porous structures are widely used in catalyst, solar cell, and molecular cognition and selection. So some attention has been paid on the preparation of porous structures [6–11]. It is very important to find a simple and inexpensive method to prepare porous semiconductor structure. It is found [12–14] that using one kind of semiconductor nanostructures as precursor, another kind of semiconductor can be synthesized by taking some chemical processing. The product made by such processing can almost preserve the precursor morphology and some of them possess a porous structure. In addition, metal oxide nanowires can be simply produced by oxidation of metal nanowires in air [15–17]. According to that, we think annealing in the air may become a good and simple way to convert 1D compound semiconductor to its corresponding porous metal oxide. Furthermore, the porous nanoribbons should be popular for better electronic conduction and mechanic stability than the nanowires.

In this paper, porous ZnO ribbons were synthesized by oxidation of ZnS ribbons at 700 °C for an hour, and the preparation method is very simple and easy to control compared with some methods. The ZnS powder and CdS powder (less than 0.05% molecular ratio), used as source materials, is much cheaper than ZnSe ever used in Ref. [15]. So this method is very suitable to obtain porous ZnO structure. Furthermore, the photoresponse of dye adsorbed porous ZnO ribbons was also studied.

2. Experimental

The synthesis of porous ZnO ribbons includes two steps. First, ZnS ribbons with smooth surfaces were grown on silicon wafers. ZnS ribbons were synthesized in an electrical furnace with a

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horizontal quartz tube (35 mm in diameter, 120 cm in length) by physical evaporation of ZnS and CdS (less than 0.05%) powder using Au catalysts. Silicon wafers were first ultrasonically cleaned in acetone and then sputter-coated with a thin (~10 nm) layer of Au film. A mixed powder of ZnS and CdS was put into the center of a horizontal tube furnace, and several clean silicon wafers coated with Au film were laid downstream of the gas flow. High purity He was introduced to the quartz tube to eliminate the oxygen inside it before heating. After about an hour, the furnace was quickly heated up to a temperature of 1100 °C and maintained that temperature for an hour while the carrier gas was introduced. After that, the power circuit was switched off and the furnace was cooled down to room temperature naturally. Finally, white product was observed on the surface of silicon wafers, which was about 6–10 cm away from the source materials. Second, ZnS ribbons were transformed to porous ZnO ribbons. The ZnS ribbons were placed in a crucible, which were loaded in an electric muffle furnace. The oxidation of ZnS was carried out at 700 °C for an hour in ambient air.

The morphology of the as-synthesized sample was characterized by scanning electron microscopy (SEM, Hitachi, S-4200). The crystal structure was analyzed by X-ray diffraction (XRD, Japan, Rigaku, D/MAX-2400) with graphite-monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The photovoltage measurements were carried out on an assembled photovoltage spectrometer using two-electrode system with light source monochromator-lock-in detection techniques (150 W Xe lamp, Zolix SBP 300 spectrometer, Stanford SR830 lock-in amplifier). All measurements were carried out at room temperature.

3. Results and discussion

The sample morphology was characterized by SEM. Fig. 1(a) and (b) show the SEM images of ZnS precursor and ZnO product ribbons. It can be seen from the images that the morphological integrity of the ribbons was kept after oxidation at 700 °C for an hour. The typical width of the ribbons varies from 2 μm to 7 μm and the length is over 100 μm on average. However, the SEM images at higher magnification shown in

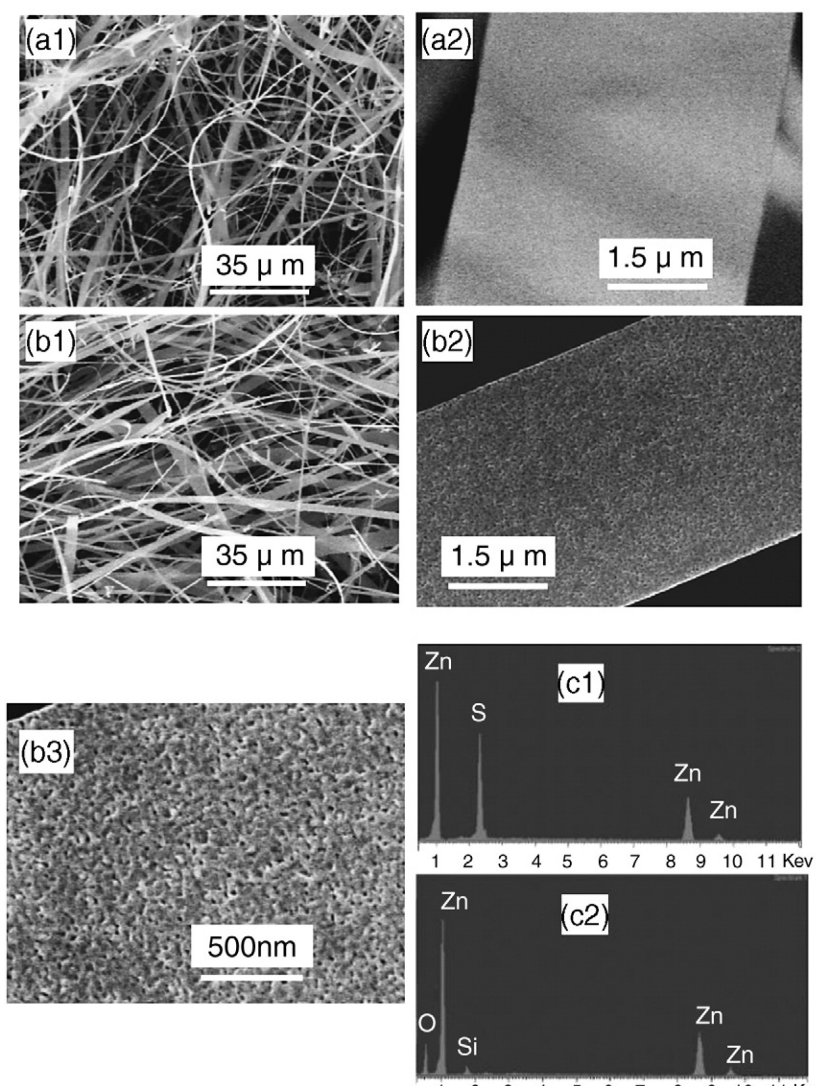

Fig. 1. SEM images of (a1) and (a2): the ZnS ribbons, (b1) to (b3): the ZnO ribbons at magnification scales and (c1) and (c2): EDX patterns of ZnS and ZnO ribbons, respectively.