

Evolution of nanowires, nanocombs, and nanosheets in oxide semiconductors with variation of processing conditions

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Abstract

The effects of processing conditions on the evolution of various sizes and shapes in the wide bandgap oxide semiconductors were studied. We synthesized various kinds of nanostructures of ZnO and SnO₂, the typical wide bandgap semiconductors for electronics and optoelectronics devices, based on a simple carbothermal reduction process. By controlling the processing temperature and the atmosphere pressure, we could obtain various kinds of nanostructures such as nanowires, nanocombs, nanorods, rod arrays, and nanosheets of ZnO.

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1. Introduction

Bottom-up approaches for nanoelectronics using nano-scale building blocks such as quantum dots, nanowires, and nanotubes have received considerable attention to date.^{1–3} Recently, one-dimensional (1D) semiconductor nanostructures have been extensively studied due to their potentials as building blocks of fabricating nano-scale devices. Various kinds of semiconductor nanowires, nanorods, and nanotubes of single element, oxide, and compound semiconductors have been successfully synthesized.^{3,4} Especially, ZnO, a wide bandgap (3.37 eV) semiconductor with large exciton binding energy (60 meV), have attracted considerable attention due to the potential applications for optoelectronics. Therefore, 1D nanostructures of ZnO including nanowires and nanotubes have been fabricated via a multitude of different routes.^{5–7}

In this study, we synthesized various types of nanostructures of ZnO and SnO₂, the typical wide bandgap semiconductors for optoelectronics, based on a simple carbothermal reduction process on the Au-coated Si substrate in controlled atmosphere pressure. By controlling the processing temperature and the atmosphere pressure, we could obtain various

kinds of nanostructures such as combs, rods, rod arrays, and sheets in addition to the typical nanowires of ZnO.

2. Experimental

Carbothermal reduction process has been widely used to fabricate various types of 1D ZnO nanostructures. As shown in Fig. 1, ZnO nanostructures involving could be fabricated nanowire, via vapor–liquid–solid (VLS) process,^{3,4} on the Au-coated Si substrate by heating the weight ratio of 1:1 mixture of ZnO and graphite in a constant flow of Ar for 5–120 min. Our objective was to investigate the effect of the supersaturation level of the source materials on the sizes and shapes of the ZnO nanostructures. When we injected the additional O₂ gas intentionally with Ar gas flow, we found that the O₂ gas facilitates the evolution of some arrayed structures of ZnO.

An equal amount of ZnO and graphite powders (99.9%, ~325 mesh) were mixed and transferred to an Al₂O₃ boat placed in the reaction tube. In the downstream of the mixed gas flow in the tube, Si substrates coated by 5–30 Å thick the Au were placed. The processing temperature varied from 800 °C to 950 °C and the amount of additional O₂ was controlled in the range of 0.5–10% with 20 sccm of Ar gas. This process had also been used for the synthesis of SnO₂ nanowires.

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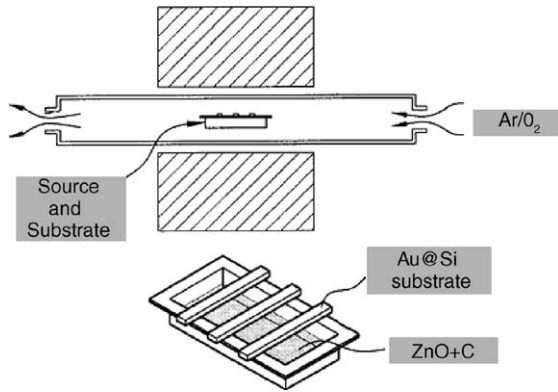


Fig. 1. Schematic illustration for the processing apparatus.

3. Results and discussion

3.1. ZnO nanowire synthesis

In carbothermal reduction process, it has been reported that ZnO nanowires can be synthesized under an inert atmosphere using Ar gas.⁴ In this study, surprisingly, we found that it is very difficult to synthesize ZnO nanowires under the flow of Ar gas only. In our experimental apparatus, the ZnO nanowires began to form on the substrate with more than 0.1% of O₂ with Ar gas. XRD confirms that ZnO nanowires have a preferred orientation of (0001) with the wurzite structure.

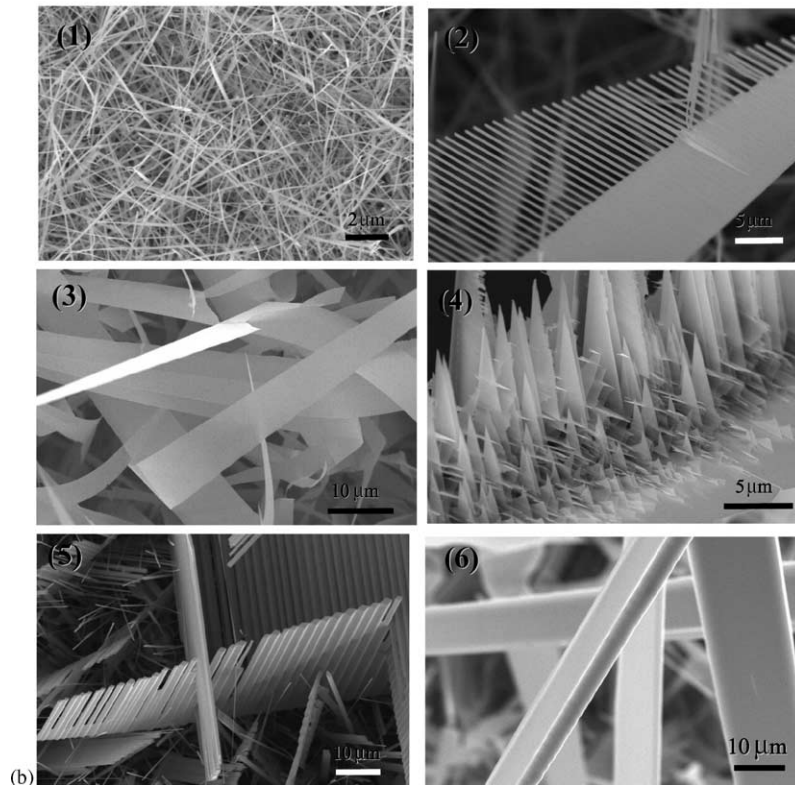
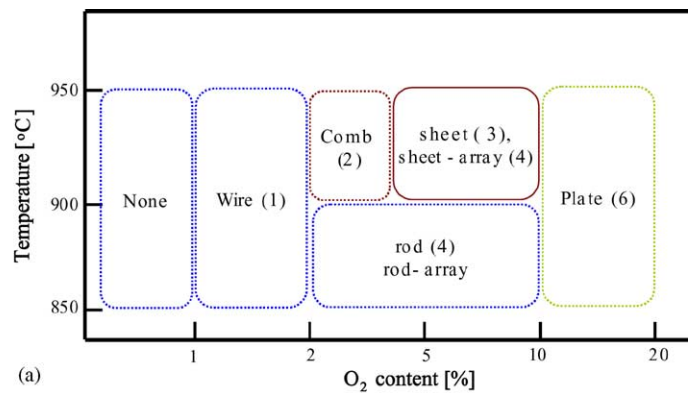


Fig. 2. (a) A summarized map of the predominant ZnO nanostructures under certain processing temperatures and oxygen contents. (b) Selected SEM images for the typical nanostructures shown in (a).

3.2. Effect of processing condition on the evolution of nanostructures

As the relative amount of O₂ gas in the flowing gas mixture increased by more than 2%, nanostructures changed from nanowires to wire-arrays, rod-arrays, and sheet-arrays. The predominant type of arrayed nanostructures under certain processing temperatures and oxygen contents can be categorized as shown in Fig. 2(a). The first micrograph image in Fig. 2(b) shows ZnO nanowires grown with 1.5% of O₂ gas. The diameter of the nanowires ranged from 50 nm to 200 nm depending on the thickness of the coated Au and the relative ratio of O₂ gas to Ar flow. The dendrite structures are highly defined nanowire arrays of a comb-like shape. The diameter of the dendritic sidebranch nanowires typically ranged from 50 nm to 300 nm and the widths the combs were in the range of 10–50 μm. The sheets are paper-like planar nanostructures and their dimensions are typically 50–300 nm in thickness and 10–100 μm in width. The plates exhibited the shapes of thick belts or square-rods in several micrometer. These nanostructures were reproducibly synthesized in the above experimental condition. Here, we noted the nanocombs and nanosheets.

As a whole, as the oxygen content and processing temperature increases, dendritic sidebranch nanowires begin to

appear along the basal nanowires. As was reported in the literatures,^{3,4} Au–Zn alloy tip moves upward leaving ZnO nanowire downward in the Au-catalyzed VLS process. In the present work, there are no evidences of Au catalyst present along the nanowires that could be confirmed by SEM and TEM-EDS analysis, and thus, the sidebranching in the Fig. 2(b) cannot be attributed to the aid of the catalyst. Therefore, this type of growth might be attributed to the diffusion-limited process in a supersaturated environment.⁸ In this case, the dendrites can be developed by the morphological instability via a vapor–solid (VS) growth mechanism without a catalyst. Thus, this is consistent with our process in which the additional oxygen facilitates the large supersaturation and the fast condensation compared with the conventional carbothermal reduction process. Meanwhile, when the width and the thickness of the sheets are in the range of 50–100 μm and 50–100 nm, respectively, the width-to-thickness ratio of the sheets reaches up to one thousand, i.e. the aspect ratio of a writing paper. Although there have been a few reports on nanobelts and nanoribbons, whose widths were several hundreds of nanometers and the width-to-thickness ratios were in the range of 3–10. Thus, they had been categorized as 1D nanowires with different cross-sectional shapes. The ultrawide nanosheets in this work, however, could be categorized as 2D nanostructures due to their high width-to-thickness ratios.

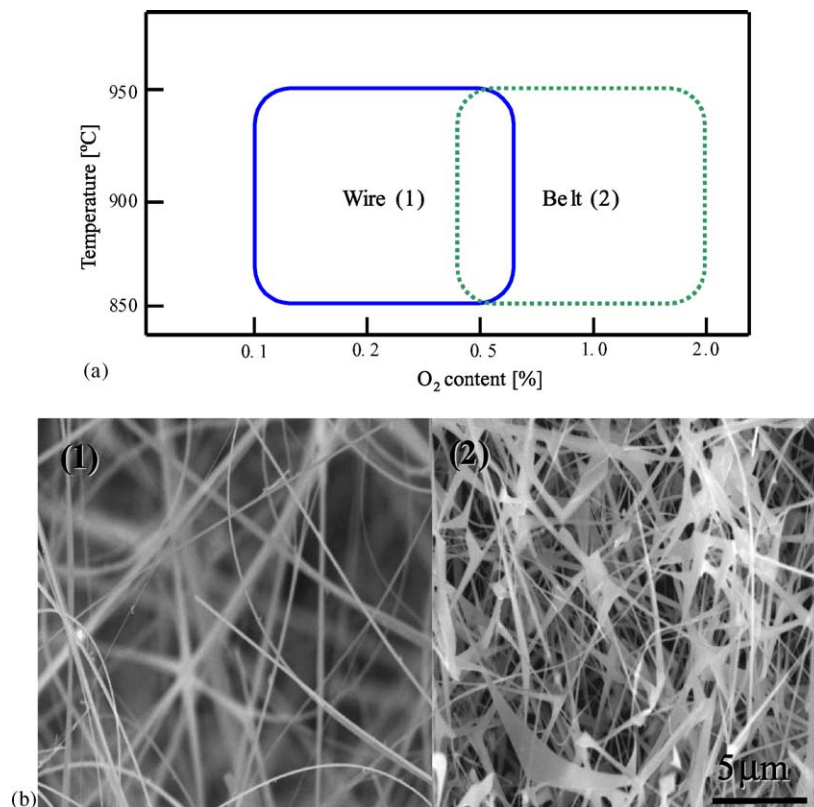


Fig. 3. (a) A summarized map of the predominant SnO₂ nanostructures under certain processing temperatures and oxygen contents. (b) Selected SEM images for the typical SnO₂ nanowires and nanoribbons.

3.3. Effect of additional oxygen gas on the synthesis of SnO₂ nanostructures

It has been reported that SnO₂ nanowires can be fabricated via the carbothermal reduction process under an inert atmosphere of Ar. In this study, we found that the amount of produced nanowires increased significantly on the substrate as the amount of O₂ increases up to 0.1% with Ar. Furthermore, as the amount of O₂ in the flowing gas mixture increased by more than 0.5%, nanostructures morphologically changed from nanowires to nanoribbons as illustrated in Fig. 3(a).

Shown in Fig. 3(b) are SEM image for SnO₂ nanowires and nanoribbons synthesized with 0.2% and 1.0% of O₂. The diameters of the nanowires ranged from 50 nm to 200 nm depending on the thickness of the coated Au and the mixed O₂ content with Ar. The widths of the ribbons are typically 100–400 nm. However, in the case of SnO₂, we could not find any combs and sheet structures as was in the case of ZnO.

4. Conclusion

In summary, the effects of processing conditions on the evolution of various sizes and shapes in the wide bandgap oxide semiconductors were studied. We synthesized various kinds of intriguing nanostructures of ZnO and SnO₂, based

on a simple carbothermal reduction process on the Au-coated silicon substrate. By controlling the processing temperatures and the atmosphere pressure, we could obtain various types of nanostructures such as combs, rods, rod arrays, and sheets in addition to the typical nanowires of ZnO. We also observed that the processing conditions are crucial parameters determining the density and diameter of the nanowires in ZnO and SnO₂.

The combs and nanosheets are monolithically single crystalline and the examples of spontaneous organization of vapor molecular species into nanoscale structures and their microscale assemblies or superlattices in one step. These kinds of arrayed structures might be useful in arrayed nano-lasers, the nanoscale electromechanical system (MEMS), arrayed sensors, and electrochemical applications.

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