Well-aligned ZnO Whiskers Prepared by Catalyst-assisted Flux Method

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Well-aligned ZnO whiskers were prepared by a catalyst-assisted flux method using ZnS powders as starting materials at a temperature of 860 °C. Au coating on the Si substrate plays a key role on the nucleation. The growth of ZnO whiskers was controlled by a high temperature SLS mechanism.

ZnO, as a wide bandgap (3.37 eV) semiconductor with large exciton binding energy (60 meV), has been used in a broad range of high-technology applications, ranging from surface acoustic wave filters, photonic crystals, light-emitting diodes, photodetectors, photodiodes, optical modulator waveguides, varistors, and gas sensors, to solar cells.[1] Because of the size and quantum confinement effects, vast interests have been devoted to grow ZnO whiskers, nanowires (nanorods, multipods or nanobelts) and nanotubes,[2–7] and ZnO nanowire array has been produced successfully by CVD,[8,9] template[10] and aqueous solution process.[1] As we know, flux method has been demonstrated to be an effective way for the synthesis of new kind of materials. NiO nanorods have been prepared by using surfactant-template-assisted thermal decomposition in NaCl flux.[11,12] Recently we developed a new route (a catalyst-assisted flux method) to synthesize well-aligned single-crystal ZnO microtube array.[13] In this paper, well-aligned ZnO whiskers was prepared by the Au catalyst-assisted flux method.

The reaction system consists of a horizontal tube furnace and quartz tube.[14] The source materials (ZnS powders mixed with NaCl) were placed in a crucible. Silicon piece (Si 100) coated with Au film (about 3 nm) was placed in the crucible about 1 cm away from the source materials. The Si piece was covered by pure NaCl flux (mp 801 °C). Then the crucible was inserted into the center of quartz tube in the horizontal tube furnace. The temperature of crucible was increased to 860 °C for 1 h and was kept at 860 °C for 4 h under a constant flow of argon at a rate of 30 standard cubic centimeters per minute. After the furnace was cooled to room temperature, the Si piece was flushed with water to remove NaCl. The morphology of the as-prepared products on Si substrate was characterized and analyzed by scanning electron microscopy (SEM) (LEO-1530) and X-ray diffraction (XRD) (Bruker D8 advance).

Figure 1 was the SEM images of as-prepared products. Figure 1a reveals that large-scale whiskers are vertically well aligned to the substrate. The length of the whiskers was about 10 um. The EDX spectra (shown in Figure 1b) demonstrate that the synthesized product was ZnO. Figure 1c is the magnified images showing a rod-like structure clearly. The diameter of the whiskesr was several tens nm to 1 um. Figure 1d was the SEM image of the whisker's front-end, the inset was the magnification of the tip. There are no metal particles on the tip.

Figure 2 shows the XRD pattern of the well-aligned ZnO whiskers. The XRD patterns show that all of the diffraction

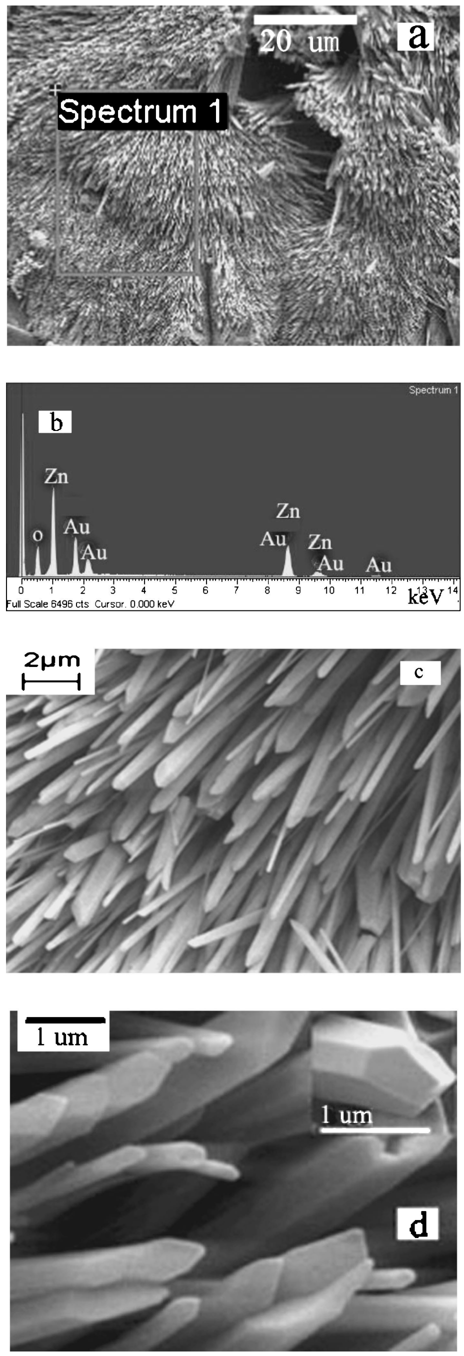

Figure 1. Typical SEM images of prepared samples. (a) the low-magnification SEM image; (b) EDX spectra of the samples; (c) the high-magnification SEM image; (d) the front-end of the whiskers.

peaks can be indexed to the hexagonal structure of ZnO. A substantially higher intensity is obtained for the [002] peak which means the ZnO whiskers grow along [001] direction.

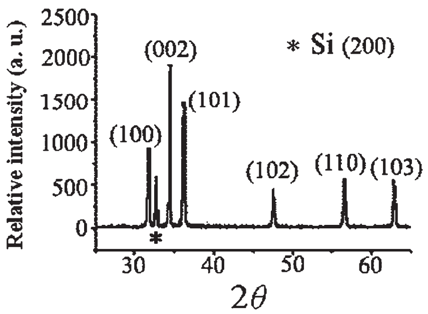

Figure 2. XRD pattern of as-prepared samples on silicon substrate.

It is well known that metals, such as Au, Ni, Fe have a profound catalytic effect on the growth of carbon nanotubes and semiconductor nanowires. Our experimental results show that no materials were grown on Si substrate without Au catalyst, which means that the growth mechanism in present work is different from the surfactant-template-assisted thermal decomposition in NaCl flux.[11,12] It is believed that Au particles and NaCl flux play a key role for the formation of ZnO whiskers. In conventional flux method, the source materials dissolved into NaCl flux first, then crystallized at suitable position.[15] On the basis of the above mentioned results and analysis, the possible growth model for ZnO whiskers may be a high temperature bottom-up SLS mechanism.[16] So we call this novel synthetic method of ZnO whiskers on Si substrate as Au catalyst-assisted flux method. ZnS was easily oxidized into ZnO at high temperature even in an inert atmosphere with traces of oxygen. In the process of the nucleation and growth of ZnO whiskers the source materials may go through three basic steps (see Figure 3): (1) Dissolution of source materials into NaCl molten salt, oxidation to ZnO, and diffusion to the interface between the NaCl flux and Au particles; (2) ZnO rod nuclei formation on the Au particles; (3) Bottom up growth of nuclei into well aligned ZnO whiskers. Of course, the detailed growth mechanism of well-aligned ZnO whiskers by Au catalyst-assisted flux method needs further study.

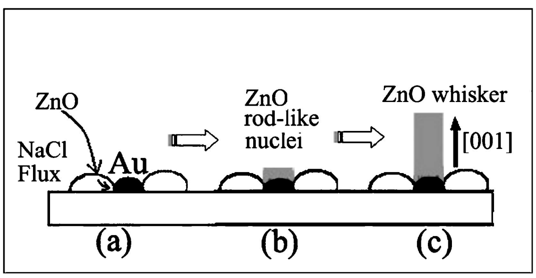

Figure 3. Schematic depiction of possible growth route for ZnO whisker: (a) dissolution of ZnS into NaCl flux, oxidation to ZnO and diffusion of ZnO to the interface between NaCl and Au particles; (b) formation of ZnO rod-like nuclei; (c) growth of ZnO whiskers.

In summary, well-aligned ZnO whiskers were prepared by a catalyst-assisted flux method. We inferred that these single-crystal ZnO whiskers could be useful in future applications including optoelectronic devices, miniature gas sensors and as substrates for photocatalysis and photovoltaics.[17] This technique can be employed to produce other metal-oxide one dimensional structure array. In addition, such a structure may also be used as a template to create three dimensional arrays of composite materials with functional architecture.[18]

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