

Articles

Oriented Attachment in Vapor: Formation of ZnO Three-Dimensional Structures by Intergrowth of ZnO Microcrystals

Zongmu Li, Faqiang Xu,* Xiuyu Sun, and Wenhua Zhang

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China

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ABSTRACT: A new setup and procedure were employed to fabricate three-dimensional (3D) complex structures of ZnO in the vapor phase following an oriented attachment mechanism developed from the solution process. Intergrowth of ZnO microcrystals has been realized through the consequent attachment of the facets of different well-defined ZnO microcrystals. Consequently, the ZnO microcrystals joined together by a specific rule, which led to a complex, 3D chain-like structure. The sufficient thermal energy in the system and the continual impacts among ZnO particles provided an environment in which the intergrowth could take place as facilely as in solutions. A strong near-bandgap emission at 382 nm indicates the excellent optical properties of oriented ZnO chains.

1. Introduction

ZnO is a wide-band semiconductor with unique optical absorption and emission properties and is one of the materials that has been intensively studied on the crystallization in nano- and micrometer scales. In addition to its applications in light-emitting displays, piezoelectricity, hydrogen storage, optical storage,¹ etc., ZnO has also been proven to be a perfect model for the crystallographic research of nano- and microcrystals by the emerging of diverse shapes and morphologies, such as nanowires,² tetrapods,³ nanobelts,⁴ hierarchical nanostructures,⁵ nanoplates,⁶ nanotubes,⁷ nanorings and nanobows,^{8,9} etc. However, although several techniques have been developed for the synthesis of inorganic materials with controlled morphologies,^{10–13} it is still a significant challenge to fabricate complex nanostructures by controlling crystalline morphology, orientation, and surface architecture. Therefore, to synthesize ZnO crystals with various sizes and special morphologies is still an important issue to exploit the unique properties of ZnO nanomaterials.

Recently, Penn and Banfield proposed a new mechanism called “oriented attachment” (OA) and found it to be a very promising route for the fabrication of complex-shaped nanostructures.^{14–17} On the basis of the OA mechanism, some structures such as single crystalline PbMoO₄ dendrites,¹⁸ anisotropic PbSe nanocrystals,¹⁹ and CdTe nanowires and ZnO nanorods^{20,21} have been synthesized up to now. However, most of the crystal growth processes so far based upon OA have been performed under hydrothermal or conventional wet chemical conditions,^{22,23}

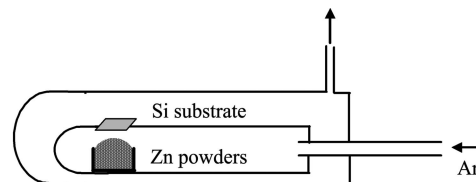


Figure 1. Schematic illustration of the experimental setup.

and complex three-dimensional (3D) structures via OA in vapor have scarcely been reported.

In this paper, we employ a new setup and procedure trying to realize the intergrowth of ZnO microcrystals based on the OA mechanism in vapor phase. Large scale of oriented complex 3D ZnO microstructures has been obtained at low temperature and under catalyst-free conditions. The dominant process for the formation of such microstructures is discussed and a mechanism is proposed.

2. Experimental Procedures

A schematic diagram of the experimental setup for the preparation of the samples is illustrated in Figure 1. The zinc powder (99.999%) was put into a self-made quartz boat, and the Si wafer which was cleaned with deionized water and acetone was placed on the outlet of the inner quartz tube and faced toward the zinc powder. The distance between the Si wafer and the zinc powder was in the range from 2 to 5 mm. After the boat was placed in the inner quartz tube in a horizontal tube furnace, a stream of Ar gas was blown through the quartz tube at the rate of 120 cm³/min for 30 min, and then the sample was gradually heated to 420 °C at a rate of 20 °C. After the temperature was

* To whom correspondence should be addressed. E-mail: fqxu@ustc.edu.cn.

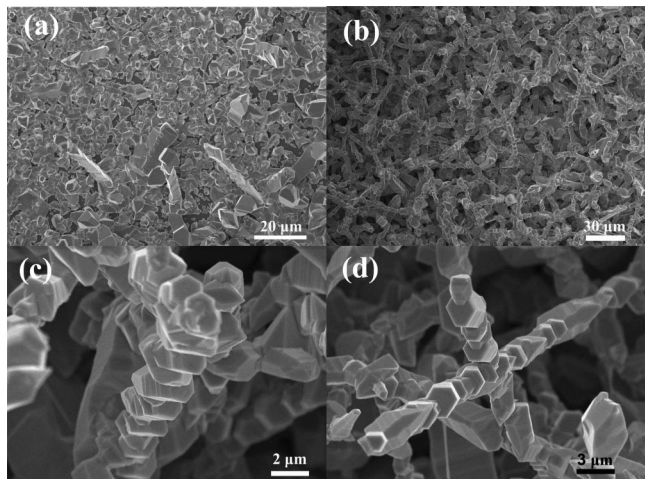


Figure 2. SEM images of oriented ZnO microstructures. (a) The initial stage of oriented attachment of ZnO crystals growth. (b) A low magnification image showing the uniformity of the 3D microstructure. (c) A microchain consisting of ZnO crystallites with irregular shapes. (d) A cross-shaped ZnO microchain composed of regular hexangular microblocks and polyhedrons.

maintained for a period of time, the furnace was cooled down to room temperature slowly, and the sample was taken out for characterization.

The photoluminescence (PL) spectrum was performed at room temperature on a LABRAM-HR (JY) spectrometer using a He-Cd laser (325 nm) as the excitation source. A JSM-6700F SEM equipped with a field emission gun was used for the high-resolution field emission scanning electron microscopy (SEM) measurements. The X-ray diffraction (XRD) data were collected on a D/max-rA diffractometer.

3. Results and Discussion

Figure 2 gives the typical SEM images of the samples. Figure 2a is an image of the sample surface obtained at 420 °C for 20 min, which indicates that a near monolayer of ZnO microcrystals has been deposited on the Si substrate randomly. The crystallites have well-defined facets and narrow size distribution, and most of them are about several micrometers. The morphology of the reaction product changed to that shown in Figure 2b after 2 h, which clearly illustrates that a large-scale and high-yield complex 3D structure has formed via the packing of the crystallites. Hundreds of crystallites intergrew together with a certain rule to form tens of micrometer chains. By comparing Figure 2, panel a with panel b, it is reasonable to infer that Figure 2a reflects the initial stage of the 3D structure in Figure 2b. The XRD pattern of the sample associated with Figure 2b is shown in Figure 3, which can be indexed to hexagonal-structured ZnO. The strong intensities and narrow full width at half maximum (FWHMs) of the diffraction peaks in the pattern imply the high purity and quality of the resulting products. Therefore, it can be said that the micrometer chains and 3D structures are composed of high-quality ZnO crystallites.

The high quality of the crystallites has also been confirmed by the PL result shown in Figure 4. As it shows, an intense PL peak centered at ~ 382 nm and a weak peak at ~ 520 nm were observed corresponding to the near bandgap edge emission and the defect emission, respectively.²⁴ The high intensity ratio of the two emissions may be attributed to the highly faceted crystallites, especially the hexangular prisms, which can serve as Fabry–Perot resonators.

Figure 2c,d shows the SEM images of two kinds of typical microchains with higher magnification in which the magnitudes of the ZnO building blocks are about 1–3 μm . It is noticeable

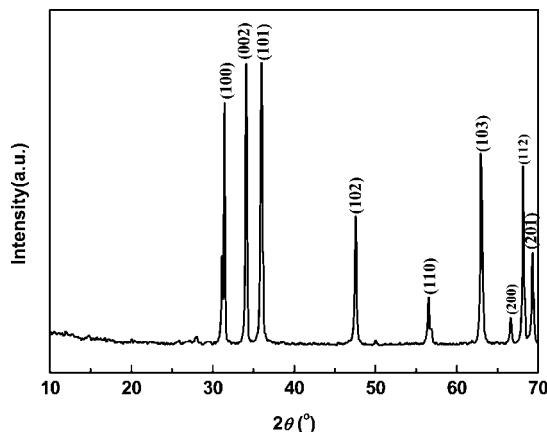


Figure 3. XRD pattern of ZnO microchains.

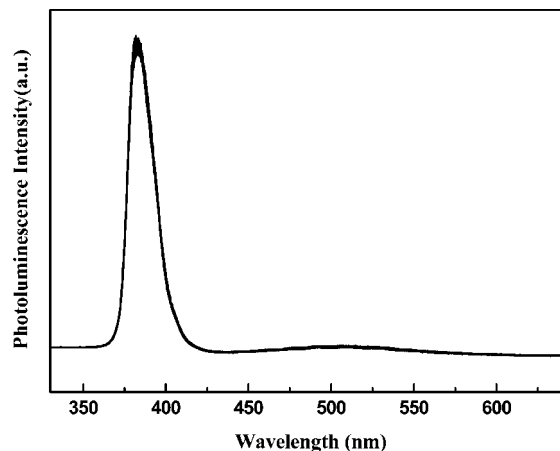


Figure 4. PL spectrum of ZnO microchains.

that although the ZnO polyhedrons in Figure 2c have irregular shapes, they look like they have the same orientation and organize in a regular way. Different from the structure in Figure 2c, most of the ZnO crystallites in the cross-shaped microchain in Figure 2d are hexangular prisms with well-defined faces and flat ends. The hexangular prisms connect at almost the same facets with each other and align along a special axis, suggesting that each chain has become an individual single crystal chemically bonded together by several blocks and not an aggregate packed randomly by crystallites.²⁵

Pacholski and co-workers suggested that ZnO is a particularly suitable candidate for the synthesis of complex 3D nanoscale building blocks using the OA method.²¹ According to the character of our products, the growth of ZnO microchains could be explained using the imperfect OA mechanism. The ZnO microcrystals have dimensionally similar surfaces, so when they meet together they will fuse along a specific direction, which is different from the random aggregation frequently observed in the literature.²⁶ The branched structures predicted by Cho et al. based on the OA process¹⁹ have been observed as shown in Figure 2d. Moreover, the intergrowth occurs at multiple sites leading to the formation of similar multibranch structures, which is also one of the key features of the OA process.²⁷

The OA mechanism plays an important role in the formation of minerals on the earth in history and in understanding the structure of artificial materials prepared in liquid media. Some authors have predicted that the OA process may be possible in cases where particles are free to move.²⁶ In nature, the formation of this kind of intergrowth product such as diamond usually

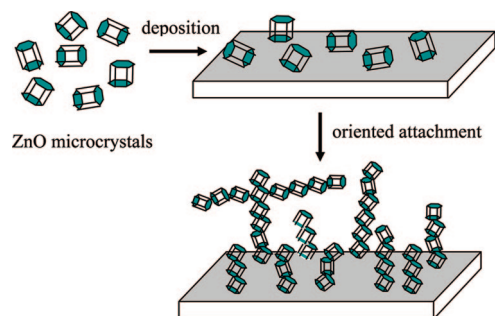


Figure 5. Schematic intergrowth process of ZnO oriented attachment in vapor.

suffers from a very complicated and long process under extreme conditions. Additionally, high pressure or surfactants are often needed in a wet chemistry method. Therefore, it is an interesting and challenging issue to synthesize intergrowth materials in a gas environment under mild conditions and to discuss the formation mechanism of such ZnO 3D microstructures, especially when taking into account the fact that the process occurred at mild temperatures and pressures.

The key characteristic of the OA process is that crystals grow along a crystallographically specific direction. Thermodynamically, the combination of the building blocks mainly relies on two factors, namely, the surface energies and the lattice matching extent of the attached surfaces. It has been found that only the facets that have the same or similar surface energies and lattice orientations can attach together because at the interface the two blocks have the same lattice stripe orientation.¹⁴ As for our experiments, the schematic of the growth stages of the ZnO microstructures are proposed in Figure 5. When the zinc powder was heated to 400–450 °C, a high zinc vapor pressure was generated because of the low evaporation temperature of zinc metal. In an atmosphere containing traces of oxygen, the evaporated “floating” zinc can be easily oxidized to produce lots of ZnO crystallites. As a result, a ZnO-rich zone was formed between the materials boat and the substrate at the equilibrium. At the initial stage of deposition, it is inevitable for the ZnO microcrystals to collide constantly with the substrate and part of them absorb to the surface. After a monolayer of ZnO crystallites was formed as shown in Figure 2a, the subsequent crystallites will deposit onto the absorbed ZnO polyhedrons. Because the absorbed ZnO crystallites possess different shapes and orientation facets, the combination probability of the succedent crystallites will depend on the surface energies and structures of the crystallites; that is to say, a suitable structure of the microcrystals is critical for the intergrowth of ZnO.²⁸ However, our results shown in Figure 2 evidently suggest that no matter whether the succedent ZnO crystallite is regular or not in shape, there will be always a suitable site for it to attach, and generally only the microcrystals with the same or similar shapes attach together. With more and more polyhedrons attaching to the existent ZnO microcrystals one by one in the same way, a chain-like structure is formed that looks like an intergrowth chain from the epitaxy of one block on the other. As the ZnO microchains are constructed, there would be a rotation between the blocks if their crystallographical orientation were not aligned to each other. The driving force of the rotation may arise from the mechanical relaxation of the highly stressed interface formed upon impact³¹ and allow the crystals to adopt a parallel orientation. Finally, with the growth and extension of the microchains from different sites, a 3D intertextured structure is formed as shown in Figure 2b,c. Because every

crystallite possesses several facets, it is not strange to find some different configurations when they attach together as seen in Figure 2c,d.

4. Conclusion

In summary, we report here a low-temperature and catalyst-free synthetic method in fabricating oriented microchains of ZnO. This intergrowth of ZnO microstructures follows an imperfect oriented attachment mechanism. The occurrence of highly anisotropic growth may be inherent in the wurtzite III–V system, which offers an opportunity for forming complex nano- or microstructures in a wide range of process conditions. The room temperature PL spectrum of the microstructures shows a narrow UV emission at 382 nm and a nearly invisible green emission at ~520 nm. We believe that these ZnO microstructures could be a new class of particular useful microstructures for crystallography and many technological applications.

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