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Research Article

Liquid Phase Morphology Control of ZnO Nanowires, Ellipse Particles, Hexagonal Rods, and Particle in Aqueous Solutions

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Liquid phase morphology control of ZnO crystals was realized with simple aqueous solution system. ZnO nanowires were successfully fabricated at 50°C. They were over 50 μm in length and about 100 nm in width. Aspect ratio was estimated to be over 500. They had no branches and were obtained without aggregations. Curved nano-wires clearly indicated high flexibility and high mechanical strength. Additionally, ellipse particles, hexagonal rods and particles were fabricated in the solutions. Morphology, crystal growth speed, and preferred growth faces were well-controlled by precise adjustment of growth conditions.

1. Introduction

Metal oxides have been used for electronic devices, optoelectronic device, and so forth. They will further expand beyond the present borders of research area. Especially, expectations for metal oxide nanostructures have increased recently for future applications. Syntheses of novel metal oxide nanostructures and development of their applications are under intense investigation [1–8]. Special issues [9], reviews [10–13], and books [14] on applications of metal oxide nanostructures have received a great response.

ZnO has attracted much attention as varistors [15], piezoelectric devices [16], electroacoustic transducers [17], and highly transparent conducting windows for solar cells, displays [18], vacuum fluorescent displays (VFDs) [19], field emission displays (FEDs) [20], electroluminescent displays (ELDs) [21], UV light-emitting diodes (LEDs), laser diodes [22], and gas sensors [23, 24], dye-sensitized solar cells [25–29], and molecular sensors [30].

Novel ZnO nanostructures are eagerly anticipated for the applications [31–34]. ZnO nanowires especially are required for luminescent devices, dye-sensitized solar cells and high sensitive sensors. The nanowires have high electrical conductivity along the longer direction. They have large surface area due to high aspect ratio of the shape. High flexibility and high mechanical strength are required to apply for the devices.

Recently, several ZnO nano-/microstructures were prepared in the solutions [34–39]. Patterning of them was realized on self-assembled monolayers (SAMs) [35]. Hydrophobic surface of SAMs accelerated deposition of ZnO nanostructures rather than hydrophilic silanol group surfaces [35]. These studies contributed development of future ZnO devices.

In this study, ZnO nanowires were developed in aqueous solutions. Anisotropic crystal growth of ZnO was well-controlled by precise adjustment of solution conditions. Additionally, ellipse particles, hexagonal rods, and particles were fabricated.

2. Experimental Details

Octadecyltrichlorosilane (OTS, $C_{18}H_{37}SiCl_3$, Acros Organics), anhydrous toluene (Aldrich Chemical Co., Inc.), zinc acetate ($Zn(CH_3COO)_2$, Kishida Chemical Co., Ltd.), ammonia (28% solution, Kishida), NaOH, HCI, ethanol, and acetone were used as received. Distilled water was used as a solvent.

An Si wafer (p-type Si [100], NK Platz Co., Ltd.) was sonicated for 10 min in water, ethanol, or acetone, in that order. It was exposed for 15 min to UV light (184.9 nm and 253.7 nm) (low-pressure mercury lamp 200 W, PL21-200, 15 mW/cm^2 for 254 nm, SEN Lights Co.) to clean the surface. UV light which has been used in this study (PL21-200) had stronger power than that we used in former studies (NL-UV253, Nippon Laser and Electronics Lab.) [40–44]. SAMs of octadecyltrichlorosilane (OTS, $C_{18}H_{37}SiCl_3$) were prepared by immersing Si substrates in anhydrous toluene (Aldrich Chemical Co., Inc.) solutions containing 1 vol% OTS (Acros Organics) for 15 min under an N_2 atmosphere. The substrates with the SAMs were baked at 120°C for 5 min to remove residual solvents and promote chemisorption of the SAMs.

Morphology of ZnO was evaluated with a scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.). Crystal structure of ZnO was evaluated with an X-ray diffractometer (XRD; RINT-2100, Rigaku, in-plane X-ray diffraction profiles) with CuKα radiation (40 kV, 30 mA) and Ni filter plus a graphite monochromator.

3. Results and Discussion

3.1. Synthesis of ZnO in Aqueous Solutions

(1) Wires. Zinc acetate ($Zn(CH_3COO)_2$, 1.375 g) was dissolved into water of 100 mL at 50°C. Ammonia (28% solution, Kishida, 910 mL) was then added as complexing agent with stirring to be $[NH_3]/[Zn] = 2.0$. The solutions showed pH = 6.99 at 1 min after addition of ammonia. The substrates were immersed in the solutions at bottom up for 3 h. The pH of the solutions was still pH = 6.99 at 3 h after immersion of the substrates.

(2) Ellipse Particles. The solutions were diluted by 4% (concentration: 1/25) for fabrication of ellipse particles.

(3) Hexagonal Rods. The solutions were diluted by 20% (concentration: 1/5) for fabrication of hexagonal rods. HCI was added to control pH.

(4) Particles. The solutions were diluted by 20% (concentration: 1/5) for fabrication of particles. NaOH was added to control pH.

ZnO was formed in the aqueous solutions as follows:

$$\begin{aligned} 2NH_3 + 2H_2O &\rightleftarrows 2NH_4^+ + 2OH^- \\ Zn(CH_3COO)_2 + 4NH_4^+ &\rightleftarrows Zn(NH_3)_4^{2+} + 2CH_3COOH \\ H_2O &\rightleftarrows OH^- + H^+ \\ Zn(NH_3)_4^{2+} + 2OH^- &\longrightarrow ZnO + H_2O + 4NH_3 \end{aligned} \quad (1)$$

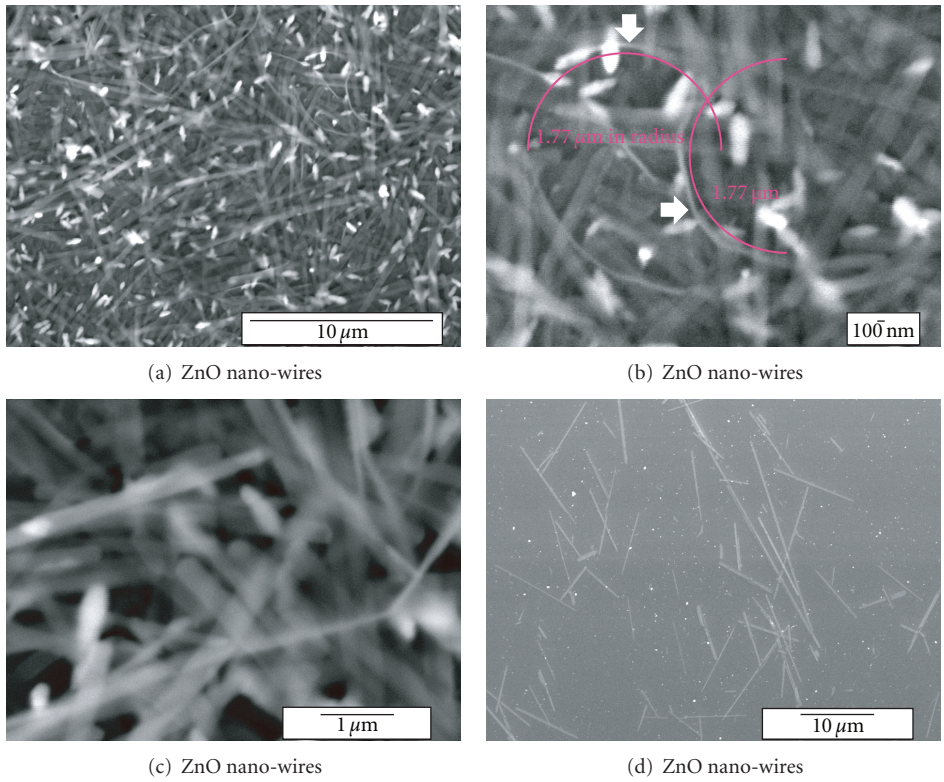
Zinc acetate solutions were transparent. The solutions became slightly white after addition of ammonia. High ion concentration proceeded formation of ZnO. The particles were formed in the solutions by consumption of ions. Supersaturation degree decreased with the decrease of ion concentrations. The solutions became transparent after a few hours.

(1) Wires. The substrates were rinsed with distilled water and dried in air after immersion. They were evaluated with SEM and XRD. XRD showed that precipitated nano-wires were single phase of ZnO without additional phases. Many ZnO nano-wires were observed on the substrates (Figures 1(a)–1(d)). Length was over 50 μm. Width was about 100 nm. Aspect ratio was estimated to be over 500 (= 50 μm/100 nm). Some nanowires curved in top right region of Figure 1(a). Magnified image was shown as Figure 1(b). Radius of the curves was about 1.77 μm (Figure 1(b)). It indicated high flexibility and high mechanical strength of the nanowires. They grew along *c*-axis of wurtzite crystal structure. High crystallinity allowed forming 1D structure with uniform width, long length, high flexibility, and high strength. Morphology and size in different areas were shown in Figure 1(c). Small amount of the nanowires deposited on a substrate (Figure 1(d)).This image indicated that the nano-wires were not aggregated and had no branches. They were obtained as separated nanowires. For comparison, ZnO 1D structures were prepared on fluorine doped tin oxide substrates in aqueous solutions. The solutions contained zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 15 mM) and ethylenediamine ($H_2NCH_2CH_2NH_2$, 15 mM). They were kept at 60°C for 6 h (Figure 2) [45]. Electron diffraction pattern indicated that the structure was a single crystal of ZnO. Lengthwise direction was parallel to *c*-axis of ZnO. Anisotropic crystal growth of ZnO along *c*-axis caused anisotropic 1D structure.

(2) Ellipse Particles. Zinc acetate (0.055 g) was dissolved into water of 100 mL at 50°C. Ammonia (36.4 mL) was then added as complexing agent with stirring to be $[NH_3]/[Zn] = 2.0$. Concentrations of zinc acetate and ammonia were 1/25 of the solution for nanowires. The solutions had low ion concentrations and low supersaturation degree. These induced slow crystallization speed. The solutions showed pH = 7.49 at 1 min after addition of ammonia. The substrates were immersed in the solutions at bottom up for 3 h. The pH of the solutions was pH = 6.87 at 3 h after immersion of the substrates.

XRD showed that precipitated ellipse particles were single phase of ZnO. Any additional phase was not detected. Many ZnO ellipse particles were observed on the substrates (Figure 3(a)). They were about 800 nm in length and 400 nm in width. Aspect ratio was estimated to be 2 (= 800 nm/400 nm). The ellipse particle had two sharp tips and rounded body. For comparison, similar ellipse particles were obtained in our previous study [35]. The previous ellipse particles had more rounded tips.

(3) Hexagonal Rods. HCI (1.0 mL) was added into water of 100 mL at 50°C. Zinc acetate (0.275 g) and ammonia (182 mL) were then added with stirring to be $[NH_3]/[Zn] = 2.0$. Concentrations of zinc acetate and ammonia were 1/5 of the solution for nanowires. The solutions showed pH = 6.87



(a) ZnO nano-wires (b) ZnO nano-wires

(c) ZnO nano-wires (d) ZnO nano-wires

Figure 1: SEM micrographs of ZnO nanowires. (a) Some nanowires in top right region curved. (b,c) Magnified area of (a) showing morphology of the wires. (d) Separated straight wires on a substrate. This image indicated that the nano-wires were not aggregated and had no branches.

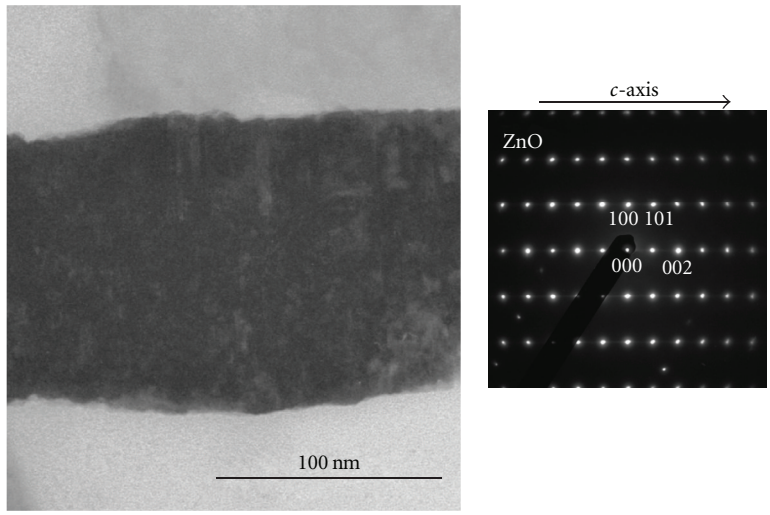
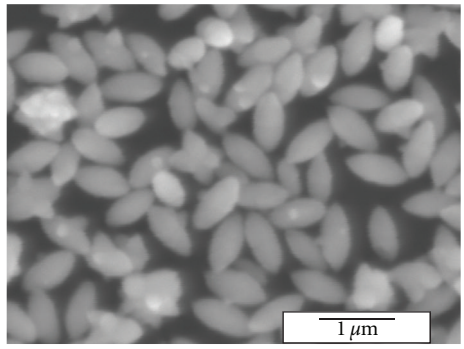


Figure 2: TEM micrograph and electron diffraction pattern of ZnO 1D structure.

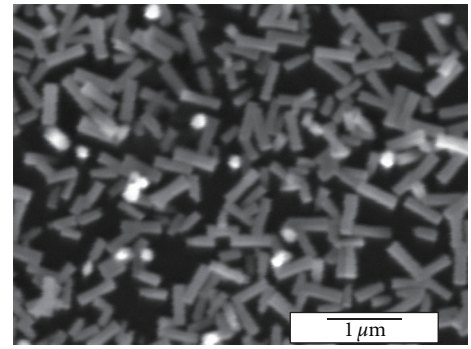
at 1 min after addition of ammonia. The substrates were immersed in the solutions at bottom up for 3 h. The pH of the solutions was pH = 6.72 at 3 h after immersion of the substrates.

XRD showed that precipitated hexagonal rods were single phase of ZnO without additional phases. Many ZnO hexagonal rods were observed on the substrates (Figure 3(b)). They were about 500 nm in length and 200 nm in width. Aspect ratio was estimated to be 2.5 (= 500 nm/200 nm). For comparison, hexagonal cylinder particles were also prepared in our previous studies [35, 36]. The aspect ratio and sizes were slightly different due to difference in synthesis conditions.

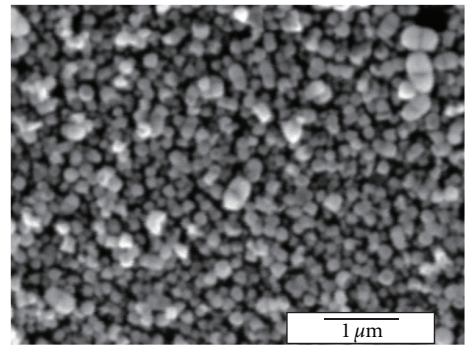
(4) Particles. NaOH (1.0 mL) was added into water of 100 mL at 50°C. Zinc acetate (0.275 g) and ammonia (182 mL) were



(a) ZnO ellipse particles



(b) ZnO hexagonal rods



(c) ZnO particles

Figure 3: SEM micrographs of (a) ZnO ellipse particles, (b) ZnO hexagonal rods, and (c) ZnO particles.

then added with stirring to be $[NH_3]/[Zn] = 2.0$. Concentrations of zinc acetate and ammonia were same to those of the solution for hexagonal rods. These solutions showed pH = 7.39 at 1 min after addition of ammonia. The substrates were immersed in the solutions at bottom up for 3 h. The pH of the solutions was pH = 6.91 at 3 h after immersion of the substrates. The pH of the solutions was higher than that of the solution for hexagonal rods due to the addition of NaOH. XRD showed that precipitated particles were single phase of ZnO without additional phases. Many ZnO particles were observed on the substrates (Figure 3(c)). They were about 20 nm in size. High pH of the solutions would decrease aspect ratio of hexagonal rods to form particles.

4. Conclusions

ZnO nanowires were successfully fabricated in aqueous solutions at ordinary temperature. They were over 50 μm in length and about 100 nm in width. Aspect ratio was estimated to be over 500. They had no branches and were obtained without aggregations. Curved nanowires clearly indicated high flexibility and high mechanical strength. They can be applied to next-generation ZnO devices. Additionally, ellipse particles, hexagonal rods, and particles were obtained. The solution conditions had large affects to crystal growth of ZnO. The knowledge obtained in this study will contribute to the development of morphology control of metal oxides.

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