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Preparation of zinc oxide nanorods using pulsed laser ablation in water media at high temperature

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Abstract

ZnO columnar single crystals were formed by pulsed laser ablation in deionized water and surfactant aqueous solutions of lauryl dimethylaminoacetic acid (LDA) and cetyltrimethylammonium bromide (CTAB) at 80 °C. ZnO particles produced by laser ablation were dissolved at a higher temperature than 60 °C, and then crystalline growth to columnar structure proceeded. While large ZnO columnar crystals were obtained in deionized water, the crystals prepared in surfactant solution were smaller than those in deionized water due to inhibition of crystalline growth by surfactant adsorption on ZnO surfaces. The size of ZnO nanorods depended on how surfactant molecules adsorb on ZnO surface.

Keywords: Pulsed laser ablation in liquid; ZnO; Nanorod

1. Introduction

ZnO is a promising material with unique properties of UV emission, optical transparency, electric conductivity, and piezo electricity due to a wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [1–3]. Low-dimensional ZnO nanostructures have also attracted interest for low-voltage, short wavelength electro-optical devices and room temperature UV lasing [4–12].

Various ZnO nanostructures, such as nanobelts, nanoribbons, nanotubes, and nanorods, have been fabricated by vapor phase techniques, such as metalorganic vapor phase epitaxy (MOVPE) [13], metalorganic chemical vapor deposition (MOCVD) [14], molecular beam epitaxy (MBE) [15] and pulsed laser deposition (PLD) [16], and by solution phase processes [17–19] such as solvothermal process and impregnation method [20]. However, the preparation methods cited above involve complex procedures, sophisticated equipment, and rigorous experimental conditions. Moreover, a metal catalyst is necessary for crystalline growth in some vapor phase techniques [14,21,22]. However, these additives may be incorporated into the nanostructures as impurities and generate an unintended defect level, that affects the physical properties [13].

Here we report a new synthetic method, a pulsed laser ablation in liquid medium (PLAL) at high temperature, to prepare highly pure ZnO nanorods. Although pulsed laser ablation is generally carried out in a vacuum or in diluted gases to fabricate particles and films, active investigation into nanoparticle synthesis of noble metal and metal oxide by PLAL have also been conducted in recent years [23–29]. The advantages of the PLAL technique are (1) inexpensive equipment for controlling the ablation atmosphere, (2) simplicity of the procedure, and (3) the minimum amount of chemical species required for synthesis compared to the conventional chemical process. Our group previously reported ZnO nanoparticle preparation by the PLAL technique in various surfactant solutions at room temperature [26,30]. By extending this research we also studied the effect of liquid temperature on the products by the PLAL technique, and highly pure ZnO nanorods were successfully produced by pulsed laser ablation of Zn metal in deionized water at high temperature. We also investigated the mechanism of the crystalline formation of ZnO nanorods and the effects of temperature and surfactant on crystalline growth. To our knowledge this is the

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first report on the effect of the liquid temperature on the products by PLAL technique.

2. Experimental

2.1. Zn ablation in deionized water at various temperatures

ZnO nanostructures were prepared by pulsed laser ablation of a Zn metal plate (Furuuchi Chemical Co., Inc.; 99.9%) in deionized water. The Zn metal plate was fixed on the bottom of a glass vessel filled with 10 cm^3 of water and was ablated with the third harmonic (355 nm) of a Nd:YAG laser operated at 10 Hz with a maximum output of 3.2 J/(pulse cm^2) and pulse width of 7 ns. The laser beam was focused on the target plate surface with a beam size of 1 mm in diameter using a lens with a focal length of 250 mm. The glass vessel for ablation was placed in an aluminum block equipped with a dry hot bath to keep the temperatures at 40, 60, and 80 °C during ablation for 40 min. The suspensions obtained by PLAL at high temperatures were naturally cooled to room temperature. Aging at various temperatures in deionized water was also carried out for 40 min after Zn ablation at room temperature for comparison.

2.2. Zn ablation in surfactant aqueous solution

Zn ablation at 80 °C was also performed in aqueous solutions of two different surfactants: lauryl dimethylaminoacetic acid (LDA) (Wako Pure Chemical Industries, Ltd.) as an amphoteric surfactant (negatively charged at the end) and cetyltrimethylammonium bromide (CTAB) (Wako Pure Chemical Industries, Ltd.) as a cationic surfactant.

These suspensions, except for that with deionized water, were centrifuged at 5000 rpm to purify and concentrate the products. The suspensions were dropped onto Si substrates for X-ray diffraction (XRD) measurement and onto a carbon-coated copper grid for scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) after drying.

3. Results and discussion

3.1. Fabrication of ZnO nanostructures in deionized water

The XRD pattern of the ZnO nanostructure prepared by laser ablation in deionized water at 80 °C is shown in Fig. 1. The obtained products were crystalline in wurtzite structure. A similar spectrum was observed for that ablated at room temperature.

Figs. 2a, 2b, and 2c present SEM images of ZnO nanostructures prepared by laser ablation in deionized water at 40, 60, and 80 °C. The particles prepared by ablation at 40 °C were almost spherical and adhered to each other. This structure was similar to those prepared at room temperature in Refs. [26,30]. In contrast, particles prepared at 60 and 80 °C were observed in the small polyhedron and rod-like nanostructures. Especially large hexagonal rod-like nanostructures, about 500–600 nm long and 200 nm wide, can be observed in Fig. 2c. The size and amount of the rod-like nanostructures increased with the

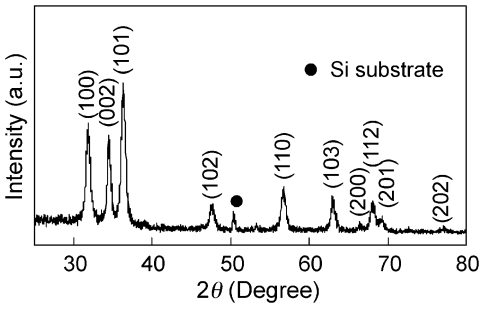


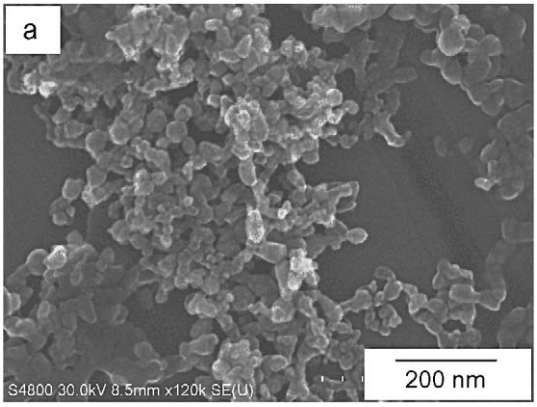
Fig. 1. X-ray powder diffraction spectrum of ZnO nanostructures prepared by pulsed laser ablation in deionized water at 80 °C.

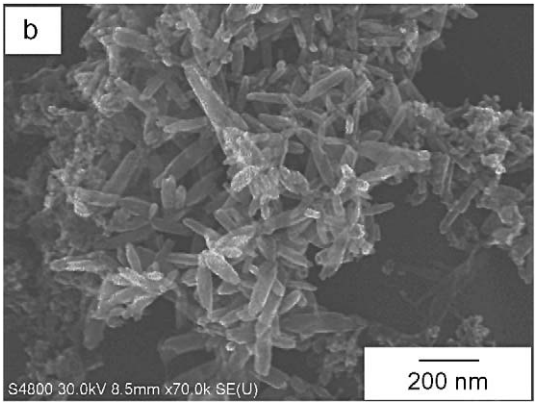
temperature during laser ablation. Flower-like structures composed of many rods were also observed at 80 °C, as indicated in Fig. 2c. Fig. 2d presents HRTEM image of the nanostructures prepared at 80 °C, with a selected area electron diffraction pattern in the inset. The nanorods are single crystals with a lattice spacing of 2.61 Å, characteristic of the (002) planes in the hexagonal ZnO phase.

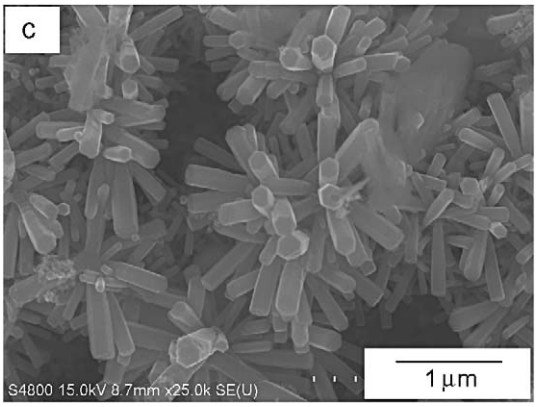
Fig. 3 shows SEM images of ZnO aged at 80 °C for 40 min after ablation at room temperature. Hexagonal rod-like nanostructures were observed after aging at 80 °C, even though spherical powder-like ZnO structures were obtained just after ablation at room temperature, as reported in Refs. [26,30]. Rod-like nanostructures were observed when they were aged at temperatures exceeding 60 °C, as noted in the ablation temperature dependence on the product morphology. Thus, these results clearly indicate that a temperature higher than 60 °C is required for crystalline growth from a spherical nanoparticles into hexagonal rod-like ZnO nanostructures. Products prepared only by ablation will be ZnO or zinc hydroxide particles, and these surfaces will be soluble in water at a high temperature. Thermodynamically calculated Zn^{2+} concentrations under equilibrium condition by the dissolution of ZnO and $Zn(OH)_2$ show drastic increases at temperature higher than 60 °C [31]. This temperature range well corresponded to the formation temperature range of ZnO nanorods. Thus the Zn species dissolved in water from ZnO and/or $Zn(OH)_2$ will possibly contribute to the crystalline growth into hexagonal rod-like crystals during the cooling process. Obtained ZnO nanorods are contaminant-free crystals, because this procedure proceeds in deionized water without any chemicals.

3.2. Zn ablation in surfactant aqueous solution

Fig. 4 presents SEM images of products prepared by pulsed laser ablation at 80 °C in surfactant solutions with different concentrations. Rod-like large crystals were observed in both LDA and CTAB, although the crystalline products were smaller than those prepared in deionized water. This indicates that surfactants suppress crystalline growth into a columnar structure. Sharp columnar crystals were observed in the LDA aqueous solution at a concentration of 3.6×10^{-3} M (Fig. 4a), whereas short columns and particles were observed at 1.8×10^{-2} M (Fig. 4b). This size decrease with an increase of LDA concentration may be due to the strong electrostatic interaction be-







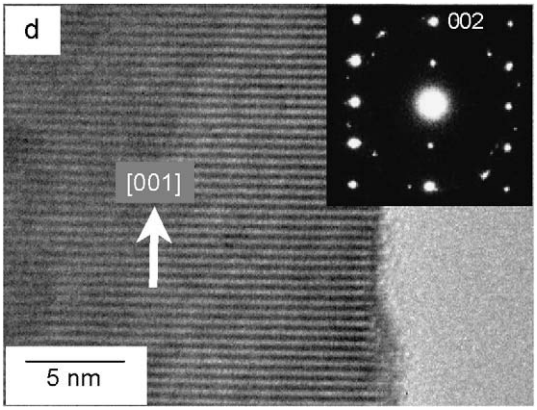


Fig. 2. SEM images of ZnO nanostructures prepared by pulsed laser ablation in deionized water at (a) 40 °C, (b) 60 °C, and (c) 80 °C and (d) HRTEM images and selected area electron diffraction pattern of ZnO prepared at 80 °C.

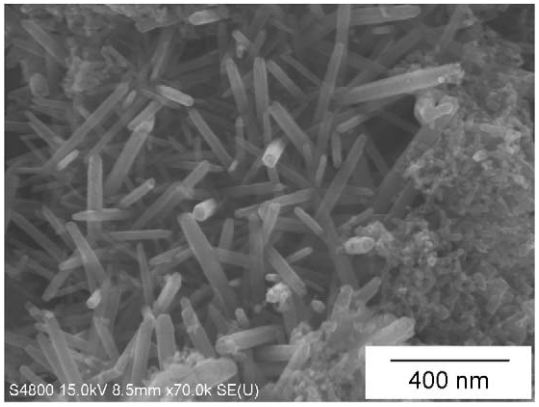


Fig. 3. SEM images of ZnO nanostructures aged at 80 °C for 40 min after ablation at room temperature.

tween the negatively charged functional group at the end of the LDA molecule and the positively charged surfaces of the ZnO particles produced by ablation. This strong interaction suppresses dissolution of the ZnO particles that feeds crystalline growth or inhibits adsorption of dissolved Zn species on the ZnO particle surfaces for crystalline growth. In contrast, sharp columnar crystals were always observed in CTAB within our test concentration range of 1.4×10^{-3} to 0.14 M. Both CTAB in water and ZnO particle surfaces in this pH region (5.6–6.8) were positively charged. Therefore, the electrostatic interaction between ZnO and CTAB is not dominant, leading to a weak interaction between ZnO and the nonpolar hydrophobic part of CTAB, which probably directs the hydrophilic group outward to the water due to hydrophobic interaction [32]. A trace of Br was detected by XPS measurement of ZnO product obtained in CTAB solution after sufficient purification, indicating the interaction between ZnO and CTAB. The weak interaction easily decreases its effect with a temperature increase because of the thermal vibration of CTAB molecules, resulting in a minor CTAB concentration dependence that differs from that observed with LDA. Thus, the surfactant effects on crystalline growth to columnar structures can be interpreted in terms of the adsorption properties.

4. Summary

In conclusion, ZnO columnar crystals were formed by pulsed laser ablation of Zn in deionized water at 80 °C. ZnO small particles were possibly produced by ablation even at a high temperature, as with ablation at room temperature. These particles were dissolved in water at a higher temperature than 60 °C, and then crystalline growth to a columnar structure proceeded. The ZnO nanorods produced in deionized water were highly pure, because only Zn metal target and water were used for preparation. Thus PLAL is a useful technique for pure material fabrication.

Surfactants inhibited the columnar crystalline growth due to their adsorption on surfaces of the ZnO species. LDA, an amphoteric surfactant with an anionic part at the end, exhibited concentration dependence on the morphology and size of the columnar products. In contrast, columnar crystals were

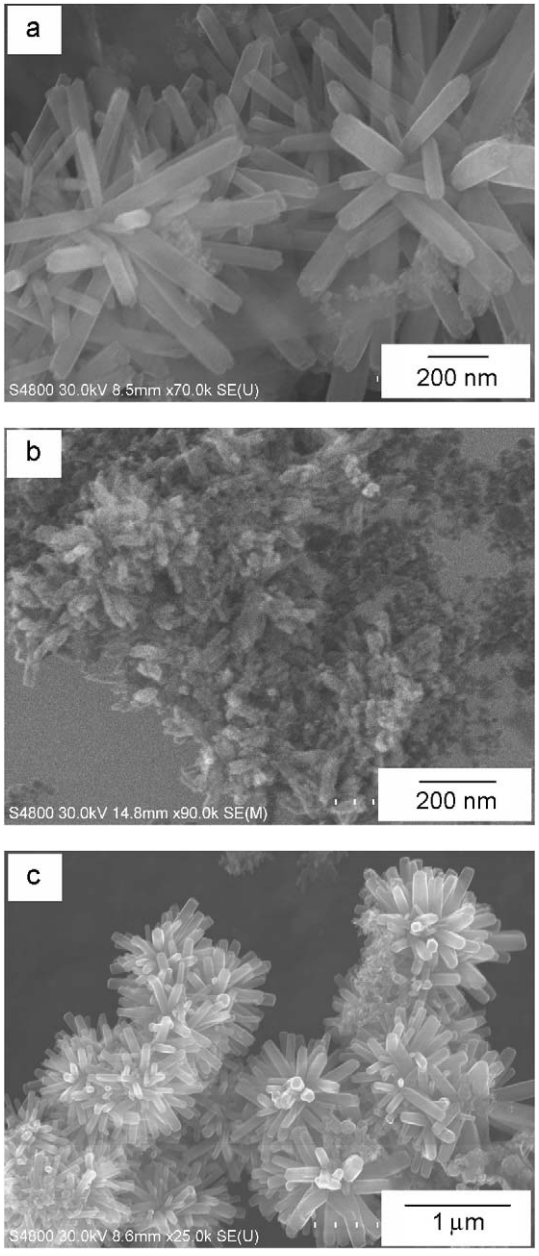


Fig. 4. SEM images of ZnO nanostructures prepared in an LDA solution at concentrations of (a) 3.6×10^{-3} M, (b) 1.8×10^{-2} M, and (c) CTAB solution at 0.14 M.

observed in any concentration of CTAB, a cationic surfactant, since the weak interaction between CTAB ions and ZnO nanoparticle surfaces partially loses its effect as a result of thermal vibration at a high temperature.

Acknowledgments

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