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Low-temperature synthesis of ZnO nanorods using organic–inorganic composite as a seed layer

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ABSTRACT

Well-aligned zinc oxide (ZnO) nanorods were synthesized using a low-temperature hydrothermal method employing a zinc/sodium dodecyl sulfate (Zn/SDS) composite as a seed layer. The results of X-ray diffraction measurements indicate that the Zn/SDS composite has a lamellar structure with an interlayer distance of 3.12 nm, which is shorter than that of the lamellar structure of SDS (3.82 nm) due to ion exchange between Zn and Na. The results of X-ray absorption fine structure analyses suggest that ZnO crystals start to grow after an induction period of 20–30 min. The length of nanorods and the aspect ratio of ZnO nanorods could be controlled by altering the molarity of ammonium and zinc nitrate in the growth solutions.

1. Introduction

Zinc oxide is an important semiconductor material, due to its direct wide band gap (3.37 eV) and high exciton binding energy (60 meV), and its application in optoelectronics, catalysts, sensors, and actuators. One-dimensional (1-D) ZnO nanostructures, such as nanobelts [1], nanotubes [2], nanohelices [3], nanorods, nanowires [4], and tower-like structures of ZnO nanocolumns [4–6] are attracting increasing research interest for application to sensing [7], optoelectronics [8], field emission [9], and piezoelectricity [10].

Numerous methods have in the past been employed to fabricate 1-D ZnO nanostructures, including thermal evaporation [1,3], chemical vapor deposition (CVD) [11–14], metal-organic chemical vapor deposition (MOCVD) [4–6,15], pulsed laser deposition (PLD) [16], radio frequency (RF) magnetron sputtering [17], template-based growth [18] and various solution-phase approaches [16,18–29]. The vertically-aligned single-crystal ZnO nanorods on R-plane-oriented Al_2O_3 (sapphire), GaN, ZnO, Ga-doped ZnO, etc., substrates were prepared by MOCVD [4–6], PLD [16], and CVD [11,14]. The growth of aligned ZnO nanorods is considered to be a good candidate for light emitting and field emissions [4–6]. However, these gas-phase approaches generally require highly sophisticated equipment, expensive single-crystalline substrates for oriented growth, and elevated temperatures of 450–900 °C, and often face other limitations, such as poor sample uniformity and low product yield [30].

Hydrothermal processes, on the other hand, permit the fabrication of large-scale aligned ZnO nanorods at relatively low cost and remarkably low temperatures without the need for metal catalysts [31,32]. However, in this process ZnO crystals layers have proved essential as the seed for the growth of ZnO nanorods, combined with calcination at above 300 °C to form ZnO crystal seed layers. Wu et al. demonstrated a one-step synthesis of oriented ZnO nanorods on an oxidized zinc foil without seed layers [33]. Although they prepared highly oriented ZnO nanorods on the surface of zinc plate, the development of low-temperature synthesis of ZnO nanorods on various substrates other than zinc-containing plate remains a challenge.

We have developed a simple method of synthesizing ZnO nanorod arrays on a Si wafer without the need for a calcination process [34,35]. This method enables the use of various substrates with low thermal stability. In this study, we used a zinc acetate/surfactant composite as a seed layer without the need for pre-heating. Several groups have reported the crystal growth of ZnO in the presence of surfactants such as sodium dodecyl sulfate (SDS) [28,36,37] and bis (2-ethylhexyl) sulfosuccinate sodium (Aerosol OT) [38]. These surfactants play a role in the control of crystal morphology and size of ZnO particles. On the other hand, in this study, we mainly expected enhanced nucleation of ZnO crystals using surfactants, rather than crystal growth. We have used a seed layer of a zinc/sodium dodecyl sulfate (Zn/SDS) composite to fabricate oriented ZnO nanorod array films. As described above, various preparation methods for ZnO nanorods have been reported. This seeding technique, however, is so far the only known method of fabricating highly oriented ZnO nanorods films at low temperatures without using ZnO crystals as a seed or ZnO substrate, and provides opportunities for applications. However, this method cannot as yet control the

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morphology of ZnO nanorod films. It is important, to be able to control the morphology, to clarify the mechanisms of nucleation and crystal growth of ZnO nanorods. In this study, we studied the structure of the zinc/surfactant composite and its effect on the nucleation of the ZnO crystals. Following this, we were able to control the aspect ratios of the ZnO nanorods by changing the compositions of the growth solutions.

2. Experiment

In a typical procedure, a solution for a seed layer was prepared from zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$:$ZnAc_2$), SDS and deionized water. The molarities of the solution were 0.2 M $ZnAc_2$ and 0.014 M SDS. The mixture was stirred for 1 h at room temperature. The solution was then spin-coated on a silicon substrate (4000 rpm, 1 min). The Zn/SDS composite was finally dried at 90 °C for 8–24 h.

The seed layer was grown to ZnO nanorods via hydrothermal synthesis. Solutions for ZnO growth were prepared by dissolving zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 28% ammonium aqueous solution (NH_3 aq) in distilled water. The molarities of the growth solutions were 0.0125–0.0375 M $Zn(NO_3)_2$ and 0.1–0.6 M NH_3. The Zn/SDS composite on the Si substrate was immersed in the above solutions in a closed vessel. The vessel was then placed in an oven at 90 °C for 0–8 h. After the growth reaction, the samples were rinsed with deionized water and then dried at 90 °C. ZnO nanorods were synthesized under the conditions listed in Table 1 and their morphology and orientation were then compared.

X-ray diffraction (XRD) patterns of the 2×2 cm films were measured using an X-ray diffractometer (RigakuMini-Flex) employing monochromatized Cu Kα with λ = 1.5418 Å in the θ–2θ Bragg–Brentano scan mode. The morphology of the sample was analyzed by field emission scanning electron microscopy (FE-SEM: Hitachi S5000 L) at an acceleration voltage of 20 kV. Zn L_3-edge X-ray absorption fine structure analyses (XAFS) were performed at the SR Center's BL-10 at Ritsumeikan University. Samples were loaded in the XAFS sample chamber under vacuum without exposure to air. XAFS spectra were obtained in the total electron yield mode.

3. Results and discussion

3.1. Effect of the solution composition for seed layer on the growth of ZnO nanorods

We have carried out a series of experiments with different solution compositions for both the seed layer and the growth of ZnO nanorods. The molarities of each component in the solutions are listed in Table 1. The FE-SEM images of the cross-section of the Zn/SDS seed layer and the film (S1) are shown in Fig. 1. The Zn/SDS composite film was a uniform 7–9 nm-thick layer. The ZnO nanorods grow in the direction of the *c*-axis, perpendicular to the surface of the Si substrate. The length of the nanorods was nearly 2 μm and their diameters were 50–100 nm.

Table 1
Molar ratios of solutions for seed layer and growth of nanorods.

	Solution for seed layer			Solution for growth solution		
Sample	SDS	$ZnAc_2$	H_2O	$Zn(NO_3)_2$	NH_3	H_2O
S1	0.069	1	280	1	17	2200
S2	0	1	280	1	17	2200
S3	0.069	0	280	1	17	2200
S4	0.069	1	280	1	4	2200
S5	0.069	1	280	1	8	2200
S6	0.069	1	280	1	13	2200
S7	0.069	1	280	1	26	2200
S8	0.069	1	280	0.5	17	2200
S9	0.069	1	280	1.5	17	2200

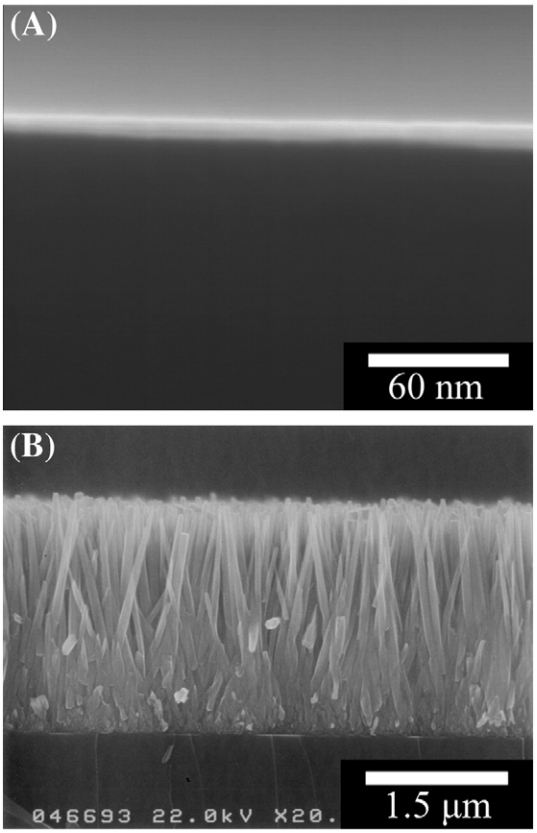

Fig. 1. FE-SEM images of (A) Zn/SDS composite layer and (B) the ZnO nanorods film. Reaction time = 4 h.

Fig. 2(A) (a) shows an XRD pattern of the film (S1) using a Zn/SDS composite as a seed layer. We evaluated the degree of *c*-orientation of the ZnO crystals on the substrates using the peak intensity ratios of the (002) plane to the (101) plane of the ZnO crystal. The (002)/(101) peak intensity ratios are plotted in Fig. 2(B). The (002)/(101) peak intensity ratio for the (S1) film is 80, much larger than that for ZnO powder (=0.4), indicating that the ZnO nanorods were highly oriented and grew perpendicularly to the surface of the Si substrate. These results are consistent with the FE-SEM observations (Fig. 1(B)). As a reference study, seed solutions without SDS (S2) and without $ZnAc_2$ (S3) were used as seed layers. The XRD patterns of the films are shown in Fig. 2(A) and (B). The intensity ratios suggest that highly oriented ZnO nanorods do not grow on the Si support if SDS or $ZnAc_2$ are not present in the seed solution.

We have previously reported that the interlayer distances of the lamellar structure of the Zn/SDS composite are 3.41 and 3.12 nm, shorter than that of SDS [35]. Schematic illustrations of the possible structures of the SDS and Zn/SDS films are shown in Fig. 3. The results of the XRD patterns suggest that Zn ions are exchanged by Na ions in SDS to form a Zn/SDS composite with a lamellar symmetry. The ion size of Zn is smaller than that of Na, and two Na ions are replaced by one Zn ion, resulting in a shorter interlayer distance after the ion exchange. As a result, Zn ions were highly dispersed in the seed layer.

Fig. 4 shows the FE-SEM images of the (S1) films synthesized at different reaction times of 0.5 and 2 h. The time courses of the length and diameter of the nanorods are plotted in Fig. 5. The diameters of the tops of the nanorods are shown in this figure. The length of the nanorods increases in proportion to reaction time. However, the diameter of the nanorods did not increase with reaction time (Fig. 5). In the early stages of crystal growth, the nanorods were relatively randomly oriented, as shown in Fig. 4(A). With a longer reaction time, however, ZnO nanorods grew selectively in the direction of