Influence of Polyethylene Glycol Addition and Strong Magnetic Field Application on Hydrothermal Synthesis of Zinc Oxide Nanorods

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Zinc oxide nano-sized rods were synthesized by a hydrothermal process to control their size and morphology. Polyethylene glycol (PEG) was used as an additive to control the particle growth by surface adsorption. Rod-shaped ZnO particles were synthesized with the addition of PEG, and the morphology changed depending on the pH of the reaction solution. At pH = 10.3–5, the size of the ZnO rods synthesized with PEG was reduced by adsorption on the whole particle. At pH > 11, the higher concentration of surface Zn–O$^-$ exposure on the (0001) plane led to the PEG preferential adsorption on the side of the ZnO hexagonal prism and the growth in the c–axis direction was promoted, so that the length of the ZnO rods increased. The addition of PEG showed the same effect on ZnO rods precipitated on the substrate. Under the strong magnetic field of 12 T, the convection flow was suppressed and the size and orientation of the ZnO rods were reduced. Even with the addition of PEG, the suppressed convection under the strong magnetic field resulted in the reduction of the size and orientation of the ZnO rods.

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1 Introduction

Zinc oxide, ZnO, with a hexagonal wurtzite-type structure has a wide range of applications, including photocatalysts, pigments, and pharmaceuticals, as well as electrical devices such as sensors, varistors, and solar cells. Depending on the synthesis method, ZnO comes in a variety of shapes and sizes, including spherical, rod, plate, wire, and elliptical needles[1),2)], and different forms of ZnO are used for different applications. A vapor phase oxidation method is used in the industrial production process of ZnO powder[3)]. In this method, metallic Zn is heated, and its vapor is oxidized to produce ZnO nano-size powders. In contrast, the liquid phase method allows the synthesis at low temperatures and has a low environmental impact. The synthesis of ZnO powders by the liquid phase method includes the homogeneous precipitation, the sol-gel and the hydrothermal methods. Among the liquid phase methods, the hydrothermal and homogeneous precipitation methods have been studied as morphology control methods for ZnO because the morphology of the fine particles can be controlled by the reaction conditions and the fine particles can be directly obtained without the need for processes such as a post heat-treatment or pulverization. In the hydrothermal method, reactions in hot water at high temperature and high pressure form a reaction field suitable for ionic reactions, resulting in high reaction rates. In most hydrothermal syntheses, crystals of high crystallinity and uniformity are directly obtained as the reaction proceeds and crystallizes by dissolution and precipitation, making it a suitable method for synthesizing particles that require morphological control or microcrystalline particles.

In the hydrothermal synthesis of ZnO, zinc oxide crystals grow in an alkaline solution by the following reaction[4),5)],

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow \quad (1)$$
$$Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-} \quad (2)$$
$$[Zn(OH)_4]^{2-} \rightarrow ZnO \downarrow + 2H_2O + 2OH^- \quad (3)$$

First, the precipitate of $Zn(OH)_2$ is formed by the

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reaction of Zn^{2+} and OH^- in solution. By heating the mixture or adding more OH^-, $Zn(OH)_2$ dissolves and $[Zn(OH)_4]^{2-}$ (tetrahydroxozincate ion) is formed. Further dehydration of $[Zn(OH)_4]^{2-}$ results in the formation of ZnO nuclei. The crystal growth then proceeds by direct bonding of ZnO and $[Zn(OH)_4]^{2-}$ by dehydration. The crystal growth of ZnO by these reactions preferentially proceeds in the c–axis direction in the absence of additives. This is because the growth rate differs for each crystal face. The growth rates are in the order, $V_{\langle 0001\rangle} > V_{\langle 01\bar{1}0\rangle} > V_{\langle 01\bar{1}1\rangle} > V_{\langle 000\bar{1}\rangle}$[6]. This results in hexagonal columnar or rod-shaped crystals grown in the c–axis direction.

Liquid phase synthesis with additives is often employed to synthesize ceramic particles with the aim of controlling their morphology. During crystal growth in solution, the additive adsorbs onto a specific crystal face and promotes or inhibits crystal growth on that face, thereby changing the crystal morphology. The morphology of fine particles is changed by selecting the additive used and adjusting the other solution conditions. Many additives have been used for the hydrothermal syntheses of ZnO, including polyvinylpyrrolidone, polyethyleneimine, polyacrylic acid, diaminopropane and sodium oleate. In this study, we focused on polyethylene glycol (PEG) as an additive that is soluble in water and remains unaltered in basic solutions. Polyethylene glycol is a polymer compound with the general formula $HO–(CH_2–CH_2–O)_n–H$ having a uniform and ordered chain structure that is easily adsorbed on the surface of metal oxide particles[7]. It is used as a dispersant for ceramic particles, where adsorption occurs by hydrogen bonding between the O atoms of PEG and –Zn–OH[10),11]. For its use as a dispersant, a study was conducted to compare the amount of PEG adsorbed in suspensions of varying pHs[11]. It was reported that the amount of PEG adsorbed on the ZnO surface decreased as the ZnO surface changed to $–Zn–OH^{2+}$, –Zn–OH, and $–Zn–O^-$ with the increasing pH. As an additive for particle synthesis, the change in the molecular weight and the PEG concentration resulted in the formation of variable morphologies including tube[8], cone[8], wire[9] and rod[10]. In this study, a hydrothermal synthesis with PEG was performed in solutions with varying pHs to investigate how the amount of PEG adsorbed or the adsorption surface is changed by changing the pH and how this changes the morphology of ZnO.

In recent years, there has been a great deal of research into the creation of materials and process control under high magnetic fields. Orientation control of ceramic materials using magneto crystalline anisotropy is one such example. Materials with an asymmetric crystal structure have a direction that is easy to magnetize (high magnetic susceptibility) and a direction that is hard to magnetize (low magnetic susceptibility) with respect to the crystal axis, and this magnetic property is called magneto crystalline anisotropy[11]. When particles with crystalline magnetic anisotropy are placed in a magnetic field, the force acting in a stable direction causes the particles to rotate so that the crystal axis with a high magnetic susceptibility is parallel to the magnetic field[12]. The synthesis under a high magnetic field could affect the orientation and morphology of the ZnO. The magnetic susceptibility of ZnO in the a and b axes is higher than that in the c axis direction[13]. Although the natural growth direction of the ZnO crystal is the c–axis direction, the ZnO crystal would be oriented so that the magnetic field and the growth direction are parallel by changing to the a and b–axes growth.

There have been very few reports about hydrothermal synthesis in a high magnetic field. Hydrothermal synthesis of ZnO films in magnetic fields up to 800 Gauss (0.08 T) reported the improvement of crystallinity[14]. Hu et al. reported the hydrothermal synthesis of Mn– and Cr–doped ZnO under a high magnetic field of 4 T, including an increase in the amount of doping[15),16]. The effects of a high magnetic field application on the morphology and orientation of ZnO on the substrate, which are believed to be strongly affected by high magnetic fields, have not been reported.

In this study, the effects of PEG addition and the application of a high magnetic field on the growth of ZnO on substrates were evaluated by using the $Zn(OH)_2$ powder as a raw material under the conditions in which unwanted anions are removed. The influence of PEG addition was precisely evaluated on the particle growth on a seeded substrate as well as via homogeneous nucleation in the reaction solutions. The effect of magnetic field application was then investigated on the orientation and morphology of ZnO under a strong magnetic field of 12 T. Both effects were evident as changes in the orientation as well as the length, thickness and hence the aspect ratio of the rod particles grown on the substrates.

2 Experimental

2·1 Synthesis of zinc hydroxide powder

For the hydrothermal synthesis, zinc hydroxide, $(Zn(OH)_2$, was used as a precursor to avoid the influence of anions other than hydroxide ions on the crystal growth. The growth of the zinc oxide crystals proceeded by reaction (3) under basic conditions. The presence of other anions may lead to the formation of by-products as well as the effects on the crystal growth of ZnO. Four grams of zinc nitrate hexahydrate ($Zn(NO_3)\cdot 6H_2O$, special grade, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) was added to 400 ml of distilled water. The solution was adjusted to pH = 7.5 using a 28% ammonia (NH_3) solution to obtain the precipitate of $Zn(OH)_2$. The precipitate was washed several times with ion-ex-

change water, filtered and dried at 55℃ for 3 hours to obtain the $Zn(OH)_2$ powder. The synthesized Zn $(OH)_2$ powder was analyzed by an X–ray Diffractometer (XRD, SmartLab, Rigaku Corp., Akishima, Tokyo, Japan) to ensure that it contained no impurities before being used in the hydrothermal synthesis.

2·2 Hydrothermal synthesis of ZnO particles via homogeneous nucleation

The hydrothermal synthesis was carried out in an autoclave consisting of a stainless steel body and a Teflon inner vessel with a maximum capacity of 50 ml. Polyethylene glycol with an average molecular weight of 2000 (Mw = 2000) was used as an additive; small molecules with Mw = 200 are unfavorable for adsorption on ZnO due to the stronger affinity of PEG with water[17], while with higher molecules of Mw = 10000 or more, the PEGs intertwine with each other to form a complex with ZnO. The use of PEG2000 was reported to assist with the formation ZnO rod-assembled microspheres[9]. Twenty-five ml of distilled water was poured into a 50–ml beaker and mixed with 0.174 g of the synthesized $Zn(OH)_2$ powder, 0.1 or 1 g of PEG (Mw = 2000) as an additive and an NH_3 solution as a pH adjuster in the appropriate quantities. After mixing, distilled water was added to bring the total volume to 35 ml. These operations resulted in a total volume of 35 ml and a $Zn(OH)_2$ concentration of 0.05 mol/L of the mixture. The prepared solution was transferred to an autoclave and heated in an oven at 180°C for 2 hours. After cooling to room temperature overnight, the product was washed with approximately 500 ml of distilled water and 200 ml of ethanol, then filtered and dried at 55°C for 2 h.

The crystalline phase of the synthesized samples was analyzed by XRD. The morphology was observed by a scanning electron microscope (SEM, S–4500, Hitachi High-Tech Corp., Tokyo, Japan). The average particle size was determined by analyzing 300 particles in the SEM images. The length and thickness of the rod-shaped particles were measured, and the aspect ratio (length/thickness) was calculated.

2·3 Hydrothermal synthesis of zinc oxide nanorods on substrate without applying a magnetic field

The deposition of zinc oxide nanorods was carried out on indium tin oxide (ITO) coated-glass substrates with ZnO seed crystals of about 100–nm thickness. Drops (0.05 mL) of zinc nitrate and hexamethylenediamine aqueous solutions, with concentrations of 0.5 mol/L, were continuously dripped onto a $10 \times 10 \times 1.1$ mm ITO substrate. After a 5–minute-stand time, spin coating was performed at 3000 rpm for 30 s, followed by heating in an oven at 300°C for 10 min.

Distilled water, 25 ml, was poured into a 50–ml beaker and mixed with 0.174 g of $Zn(OH)_2$ powder, 0.1 g of PEG and an equivalent amount of an NH_3 solution as a pH adjuster. After mixing, distilled water was added to produce a $Zn(OH)_2$ concentration of 0.05 mol/L and a total volume of 35 ml. The ITO substrate with ZnO seed crystals was placed face down, and the autoclave was heated in an oven at 120℃ or 150℃ for 2 hours. After cooling to room temperature overnight, the prepared samples were washed with distilled water and ethanol, then dried at 55°C for 2 hours.

The crystalline phase was identified by XRD, the morphology was observed by SEM and the grain size was calculated. The degree of orientation in the c–axis direction was calculated from the intensity ratio of the XRD pattern using the Lotgering method[18]. The calculation formula is as follows:

$$F = \frac{P - P_0}{1 - P_0} \times 100 \tag{4}$$

$$P_0 = \frac{\Sigma_{I(00l)}}{\Sigma_{I(hkl)}} \tag{5}$$

$$P = \frac{\Sigma_{I(00l)}}{\Sigma_{I(hkl)}} \tag{6}$$

The Lotgering factor, F, represents the degree of orientation, where $F = 100\%$ is a perfect orientation and $F = 0\%$ is a random orientation; P_0 and P represent the diffraction line intensity ratio of the c–axis in the unoriented sample and the synthesized sample, respectively.

2·4 Hydrothermal synthesis of zinc oxide nanorods on a substrate under a strong magnetic field

The synthesis under high magnetic fields was carried out in a magnetic field generator, and the autoclave has a brass body and a Teflon inner vessel with a maximum capacity of 20 ml, even smaller than that used for the synthesis without the magnetic field. As the amount of zinc in the raw solution was much greater than the amount deposited on the substrate, it was assumed that the autoclave volume had no significant effect on the particle deposition. The distilled water, 10 ml, was poured into a 20–ml beaker and mixed with the $Zn(OH)_2$ powder and NH_3 solution as the pH adjuster in the appropriate quantities. To investigate the effect of the PEG addition, the synthesis was also carried out with 0.1 g of PEG added to the raw solution. After mixing, distilled water was added to give a $Zn(OH)_2$ concentration of 0.05 mol/L and a total volume of 15 ml. The ITO substrate with ZnO seed crystals was placed in the Teflon container. The autoclave wrapped with a mantle heater was placed in a high magnetic field generator (Cryogen-free superconducting magnet, Japan Superconductor Technology, Inc., Kobe, Hyogo, Japan). The hydrothermal reaction was carried out under a magnetic field of 12 T for 2 h at a temperature of 120°C or 150°C. The direction of application of the magnetic field was perpendicular or

horizontal with respect to the substrate. After cooling to room temperature, the products on the substrate were washed with approximately 100 ml of distilled water and 50 ml of ethanol, then dried at 55 ˚C for 2 h.

3 Results and Discussion

3·1 Influence of PEG addition on hydrothermal synthesis of ZnO particles

The XRD pattern of each sample is shown in Fig. 1. A single ZnO phase was obtained for all the samples. The morphological observations by SEM are shown in Fig. 2. The average particle length, thickness and aspect ratio determined using the SEM images are summarized in Table 1.

Most of the particles were rod-shaped, and their size varied with the pH and the amount of added PEG. Comparing the samples synthesized at pH = 10.3–5, the samples with the PEG addition were smaller in both the length and thickness than those of the PEG free sample, in particular, the sample with 1 g PEG added was about 200 nm shorter in length than that of the PEG–free sample.

Table 1 Average length, thickness and aspect ratio of ZnO particles formed by homogeneous nucleation at 180℃.

Amount of PEG addition/g	pH	Average length/ nm	Average thickness/ nm	Aspect ratio
0	10.3	857 ± 347	188 ± 54	4.6
0.1	10.5	785 ± 429	164 ± 87	4.8
1	10.5	650 ± 447	145 ± 76	4.5
0	11.5	822 ± 417	177 ± 44	4.6
0.1	11.4	793 ± 446	182 ± 81	4.4
1	11.3	850 ± 548	191 ± 84	4.5
0	11.8	1016 ± 522	192 ± 81	5.3
0.1	11.9	1370 ± 806	214 ± 116	6.4
1	12.0	1339 ± 877	223 ± 100	6.0

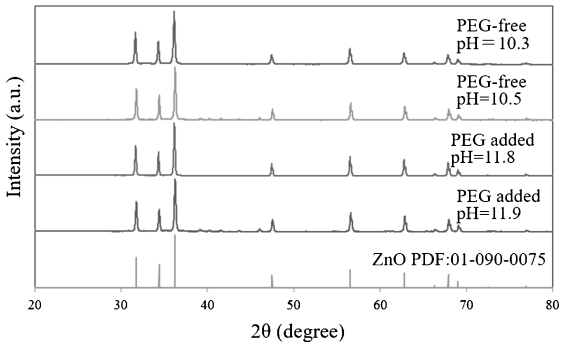

Fig. 1 XRD patterns of particles formed from zinc hydroxide solution with and without PEG additive; additive amount: 0.1 g.

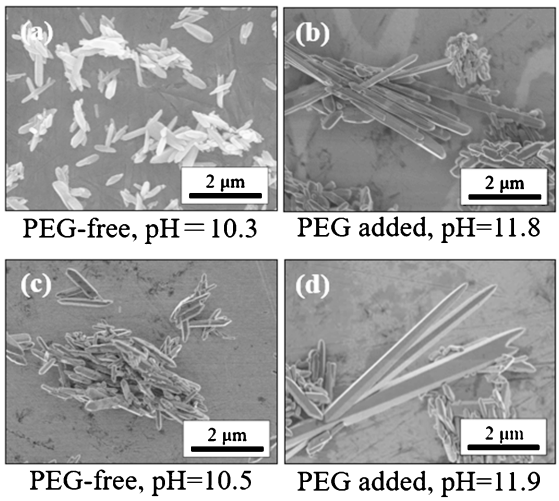

Fig. 2 SEM images of particles formed from zinc hydroxide solution with and without PEG additive; additive amount: 0.1 g.

The addition of PEG reduced both the length and thickness of the particles at pH = 10.3–5, as the adsorption of PEG suppressed the overall growth of the particles, while at pH > 11, the preferential adsorption of PEG on the sides of hexagonal prism promoted the c–axis growth, resulting in a significant increase in the particle length.

The samples synthesized at pH = 11.3–5 showed a less pronounced change than those synthesized at pH = 10.3–5. Only a slight increase in the length was observed for the sample with 0.1 g PEG added compared to the PEG–free samples. The samples synthesized at pH > 11.5 exhibited a significant increase in length compared to the samples synthesized at pH ≤ 11.5. Both samples with 0.1 and 1 g PEG added showed an increase in the length of approximately 300 nm and an increase in the aspect ratio compared to the PEG–free sample.

The variation of the particle size with pH can be summarized as follows. First, for the samples synthesized at pH = 10.3–5, the addition of PEG decreased both the length and thickness of the particles, indicating that the adsorption on the entire ZnO particles inhibited their overall growth. On the other hand, for the sample synthesized at pH > 11, the addition of PEG significantly increased the length of the particles, indicating that more PEG was adsorbed on $\{01\bar{1}0\}$, the side of the hexagonal prism, resulting in an enhanced growth in the c–axis direction.

The change in the surface adsorption with pH should be caused by the change in the ZnO surface due to OH^- in the solution. The ZnO surface state changes with the pH as follows[19],

(in basic solution)

$$-Zn-OH + OH^- \rightarrow -Zn-O^- + H_2O \quad (7)$$

It is known that metal oxide surfaces become hydrated and have OH groups when in contact with water. In the present study, the grown ZnO surface originally has OH groups because the growth of ZnO under basic conditions is caused by the binding of $[Zn(OH)_4]^{2-}$ directly onto the ZnO surface via dehydration. Under high pH conditions, this surface is deprotonated by OH^- and transformed into $-Zn-O^-$ as in reaction (5). This change is expected to preferentially occur on the (0001) surface as ZnO is polar in the c-axis direction. In other words, ZnO is expected to form more $-Zn-O^-$ on the (0001) plane in high pH solutions. The adsorption of PEG depends on the surface state and decreases in the order $-Zn-OH^{2+} > -Zn-OH > -Zn-O^-$ [11]. Therefore, during the synthesis at pH > 11, more PEG was adsorbed on the side's $\{01\bar{1}0\}$ surface than on the (0001) surface, where more $-Zn-O^-$ is present. On the other hand, during the synthesis at pH = 10.3–5, most of the surfaces are –Zn–OH because some OH^- is consumed by the synthesis reaction, thereby approaching the isoelectric point of ZnO, pH = 9.5[20]. Therefore, there is no difference in the adsorption susceptibility between the different surfaces, thus PEG would absorb throughout all the surfaces.

3·2 Influence of PEG addition on hydrothermal synthesis of zinc oxide nanorods on substrate

For the synthesis of nanorods on the substrate, the reaction conditions were pH > 11 and heating temperatures below 150°C, because the seed crystals did not grow at pH < 11 and the seed crystals dissolved at the heating temperature of 180°C, thus no ZnO nanorods were obtained on the substrate. Therefore, the reaction temperature was set to 120 and 150°C. The effect of PEG addition was investigated with a 0.1–g PEG addition.

The XRD pattern and orientation of each sample are shown in Fig. 3. Diffractions from the $(10\bar{1}0)$, (0002) and $(10\bar{1}1)$ planes of ZnO were observed together with those from the ITO substrate. Comparing the degree of orientation, the substrate synthesized with PEG had a slightly higher degree of orientation at all the synthesis temperatures.

The surface and cross-sectional SEM observations of the samples are shown in Fig. 4. The length, thickness and aspect ratio of each sample are summarized in Table 2.

The addition of PEG had the effect of significantly increasing the length and aspect ratio of the ZnO nanorods. As discussed in the previous section on the growth of the rod-shaped particles, the PEG adsorption on the side surface of the ZnO hexagonal prism would promote growth in the c-axis direction. In all the samples, rod-shaped particles were grown on the substrate. The size of the particles significantly changed with and without the addition of PEG, and the length and aspect ratio significantly increased with the addition of PEG regardless of the synthesis temperature.

At the synthesis temperature of 120°C, the sample synthesized with the PEG addition showed an increase in length by about 700 nm and in the aspect ratio by about 12 compared to those of the PEG–free sample. At the synthesis temperature of 150°C, the sample with the PEG addition showed an increase in the length of about 200 nm compared to that of the PEG–free sample, even a smaller increase compared to that in the samples prepared at 120°C.

The PEG addition resulted in a slight increase in the orientation and a significant increase in the

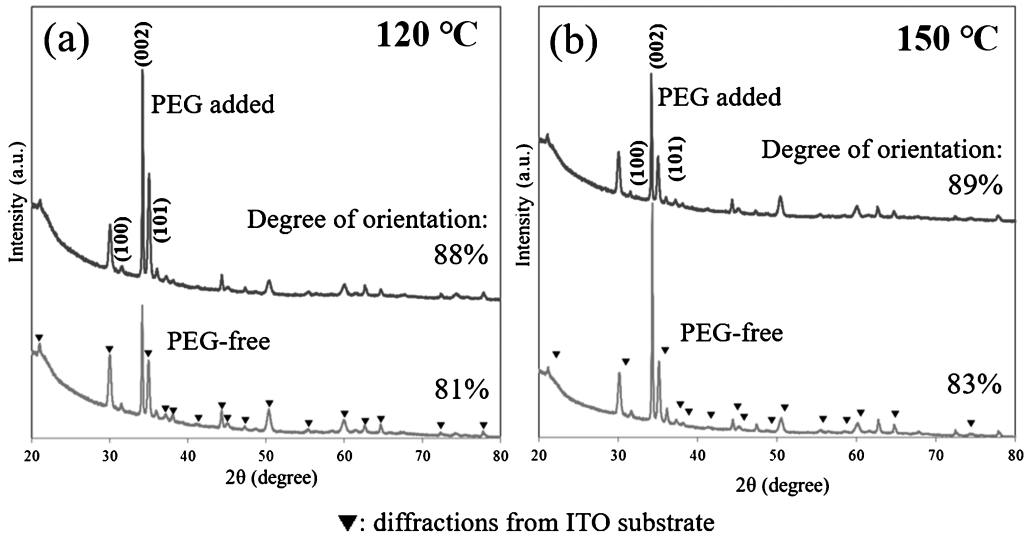

Fig. 3 XRD patterns of nanorods formed on the substrate from zinc hydroxide solution with and without PEG additive; additive amount: 0.1 g; reaction temperature: (a) 120°C, (b) 150°C.

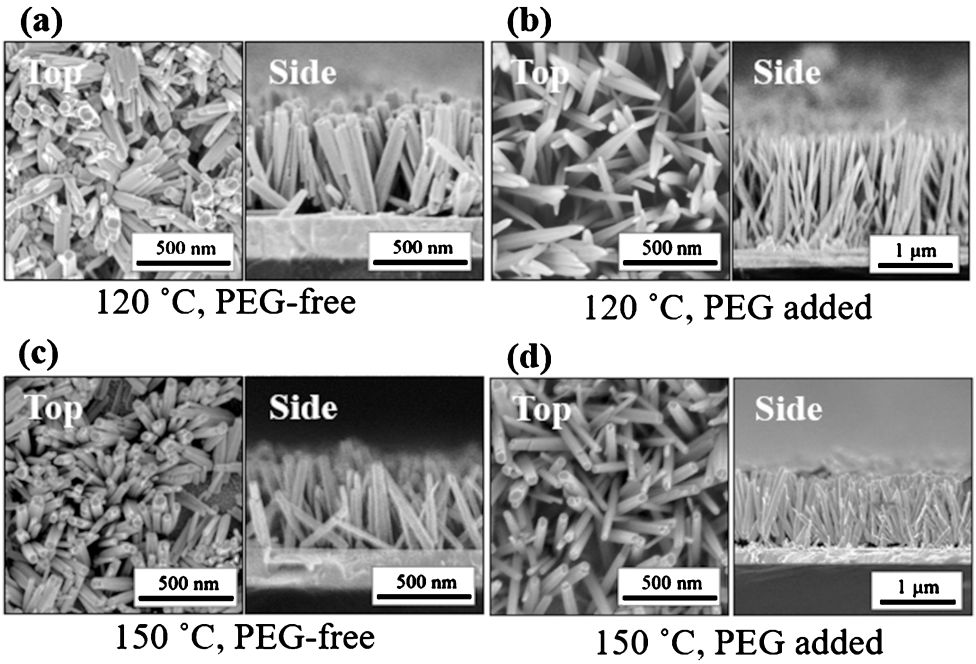

Fig. 4 SEM images of formed on the substrate from zinc hydroxide solution with and without PEG additive; additive amount: 0.1 g; reaction temperature: (a), (b) 120°C, (c), (d) 150°C.

Table 2 Average length, thickness and aspect ratio of ZnO nanorods formed on substrate without applying a magnetic field.

Temperature, °C	Amount of PEG addition/g	pH	Average length /nm	Average thickness/ nm	Aspect ratio
120	0	11.3	424±154	52±21	8.2
	0.1	11.3	1167±300	58±21	20.1
150	0	11.1	400±114	46±15	8.8
	0.1	11.3	604±231	58±20	10.5

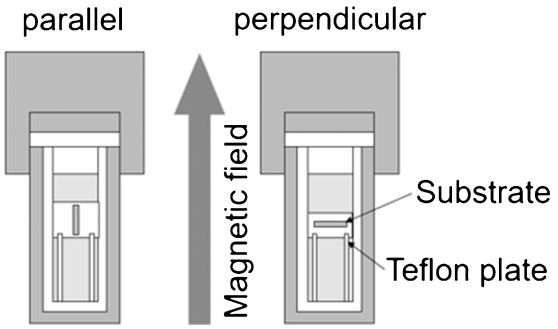

Fig. 5 Illustrations of substrate configurations: parallel or perpendicular to the magnetic field.

length and aspect ratio of the ZnO nanorods formed on the substrates. As often discussed, this should be due to the similar effect in the growth of the rod-like particles. The increase in the $Zn-O^-$ concentration on the (0001) plane under basic conditions and the consequent adsorption of more PEG addition on the side of the hexagonal prisms promoted the growth in the c-axis direction. The average length varied with the synthesis temperature; this would be due to the partial dissolution of ZnO on the substrate even at 150°C, since the seed crystals dissolved when synthesized at 180°C and no growth of ZnO took place.

3·3 Hydrothermal synthesis of zinc oxide nanorods on substrate under a strong magnetic field

The synthesis was carried out at the temperatures of 120 and 150°C under the strong magnetic field of 12 T. As shown in Fig. 5, the autoclave was set up so that the substrate was perpendicular or parallel to the magnetic field.

Figure 6 shows the XRD and orientation of each sample prepared without the PEG addition. In all the samples, diffractions from the $(10\bar{1}0)$, (0002) and $(10\bar{1}1)$ planes of ZnO were observed together with those from the ITO substrate. Comparing the diffraction line intensities with the background levels, the amount of zinc oxide formation appears to have decreased in the high magnetic fields. This effect of a high magnetic field application is discussed in detail in the latter part of this section. Focusing on the degree of orientation, we found that the samples synthesized under a magnetic field had about a 10–20% lower orientation than those synthesized without the magnetic field application at each synthesis temperature. No significant difference in the orientation of the formed nanorods was found de-

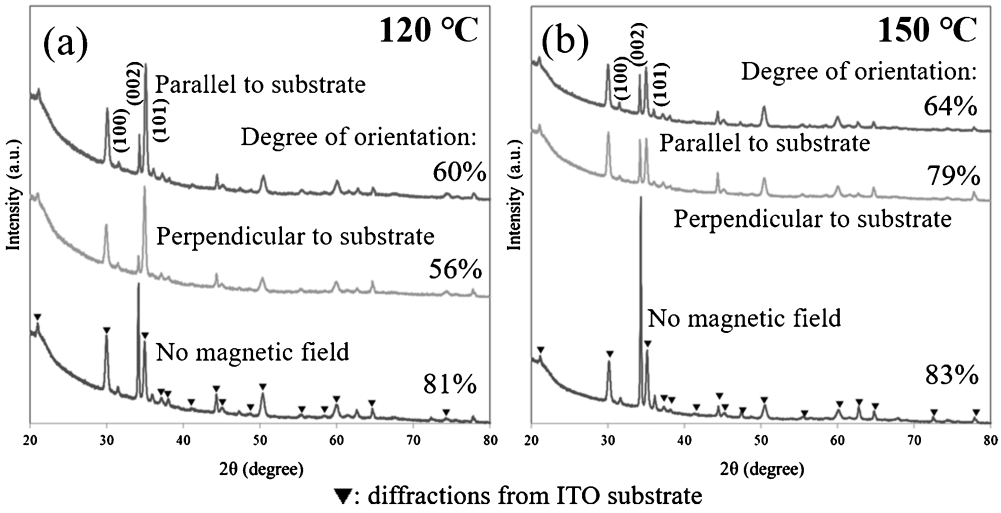

Fig. 6 XRD patterns of nanorods formed on the substrate from zinc hydroxide solution under a magnetic field of 12 T without PEG additive; reaction temperature: (a) 120°C, (b) 150°C. For comparison, XRD pattens for no magnet field are also shown at each temperature.

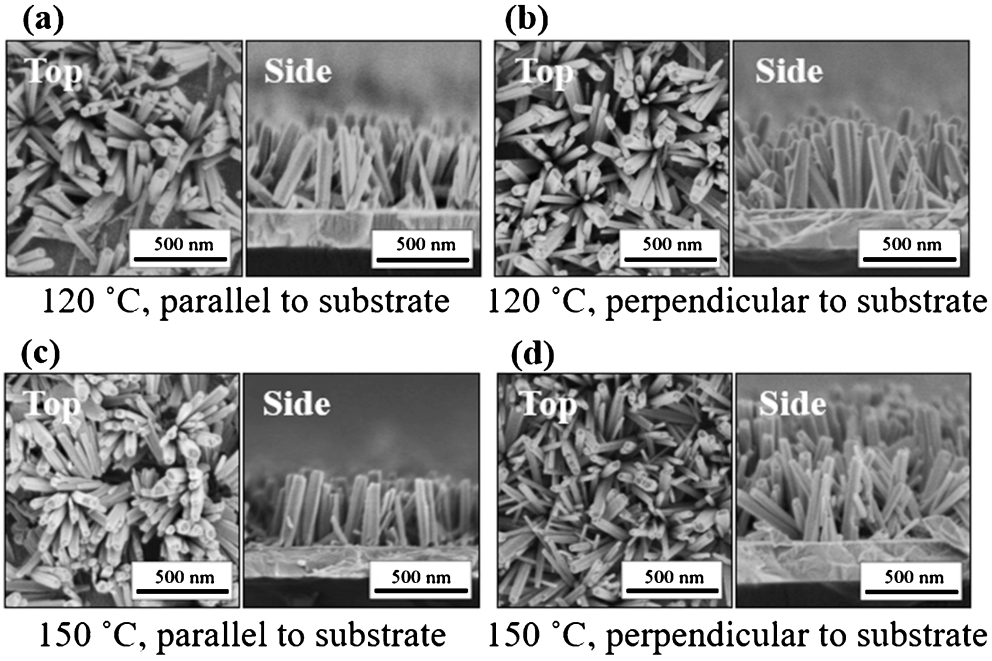

Fig. 7 SEM images nanorods formed on the substrate from zinc hydroxide solution under a magnetic field of 12 T without PEG additive; reaction temperature: (a), (b) 120°C, (c), (d) 150°C.

pending on the orientation of the substrate with respect to the magnetic field, i.e., perpendicular or parallel.

Due to the anisotropic structure of hexagonal zinc oxide, we expected to see a change in the degree of orientation, but no significant difference was observed due to the different substrate configurations. For the change in orientation of the growing crystals, the magnetic anisotropy energy induced by an external magnetic field acting on hexagonal zinc oxide with crystal anisotropy must exceed the grain boundary energy (the energy required to join free surfaces and form grain boundaries[21]). Zinc oxide is an antimagnetic material, and the magnetic susceptibility of the crystal is so small that the magnetic anisotropy energy acting on the nano-sized particles is much smaller than the grain boundary energy, and it is understood that even a strong magnetic field of 12 T was not sufficient to change the orientation of the ZnO crystal growth[11),22)].

The surface and cross-sectional SEM observations of the samples synthesized under each condition are shown in Fig. 7. The length, thickness and aspect ratio of each sample are summarized in Table 3. In

Table 3 Average length, thickness and aspect ratio of ZnO nanorods formed on substrate under a magnetic field of 12T with and without PEG addition.

PEG addition	Temperature, ℃	Directions of magnetic field with respect to substrate	pH	Average length/ nm	Average thickness/ nm	Aspect ratio
no addition	120	perpendicular	11.3	273±102	43±18	6.3
		parallel	11.3	278±108	47±18	5.9
	150	perpendicular	11.3	261±108	38±15	7.0
		parallel	11.3	368±101	42±19	8.8
with PEG addition	120	perpendicular	11.3	410±92	46±20	8.9
		parallel	11.3	241±96	44±19	5.5
	150	perpendicular	11.3	242±82	39±17	6.1
		parallel	11.3	358±128	40±13	8.9

all the samples, rod-like ZnO grew on the substrate. The size of the particles varied with and without the application of a magnetic field. At both temperatures, the length of the ZnO rod formed without application of a magnetic field was about 400 nm, whereas the length of the substrate synthesized by application of a 12–T magnetic field was reduced to about 300 nm. There were no differences in the size or morphology of the ZnO on the substrate depending on the orientation of the substrate (perpendicular or parallel) to the magnetic field.

The decreases in the particle length and orientation due to the application of a high magnetic field would be attributed to the fact that the application of the magnetic field suppressed the convection of the solution and reduced the growth rate[23),24)], and that the application of the magnetic field caused some ZnO particles to obliquely or laterally tilt. As shown in Fig. 7, observations from the top view show that all the rod-shaped particles were partially collapsed laterally.

With reference to a study, which simulated the motion of a conductive fluid containing an electrolyte under the application of a strong magnetic field, and a study, which verified the results of this analysis by means of a material growth experiment[25),26)], the following considarations can be made about the formation of zinc oxide in the present study. When the solvent and solute move together, the solution can be considered as a uniform conductive fluid. When a conductive fluid moves in a strong magnetic field, Lorentz forces are generated. This force is in a direction that prevents the conductive fluid from moving, thus suppressing convection and making it difficult for the solution to move. Crystal growth in a solution with suppressed convection is thought to be a result of the solute supply being dominated by the diffusion rate, which slows down the mass supply. The growth rate then decreases due to the reduced supply of Zn^{2+} on the substrate, leading to a reduction in the length and orientation of the rod-shaped particles.

Besides the effect of the magnetic field, another possible reason for the suppressed convection could be the difference in the autoclaves used for the syntheses with and without a magnetic field. The diameter of the autoclave used for the synthesis in a magnetic field of 12 T is smaller than that of the autoclave used for the synthesis without a magnetic field, thus, the substrate placed in the center of the vessel could block longitudinal convection.

Figure 8 shows the XRD and orientation of each sample prepared with the PEG addition. In all the samples, diffractions from the $(10\bar{1}0)$, (0002) and $(10\bar{1}1)$ planes of ZnO were observed together with those from the ITO substrate. As with the PEG–free synthesis, the amount of produced zinc oxide appears to decrease under the higher fields when the diffraction line intensities are compared with the background levels. In terms of the degree of orientation, the samples synthesized under a magnetic field had a slightly lower degree of orientation than that synthesized without a magnetic field. No significant difference in the orientation of the formed nanorods was found depending on the orientation of the substrate with respect to the magnetic field; i.e., perpendicular or parallel.

The surface and cross-sectional SEM observations of the samples synthesized under each condition are shown in Fig. 9. As shown in Table 3, at both temperatures, compared to the length of the ZnO rod formed without application of a magnetic field, that formed under the 12–T magnetic field was reduced. There was no appreciable dependency in the size or morphology of the ZnO rods regardless of the configuration of the substrate; i.e., perpendicular or parallel to the magnetic field. Unlike the size dependence of the particle formation, there was no clear PEG addition effect. Even with the addition of PEG, the size reduction effect of the magnetic field appli-

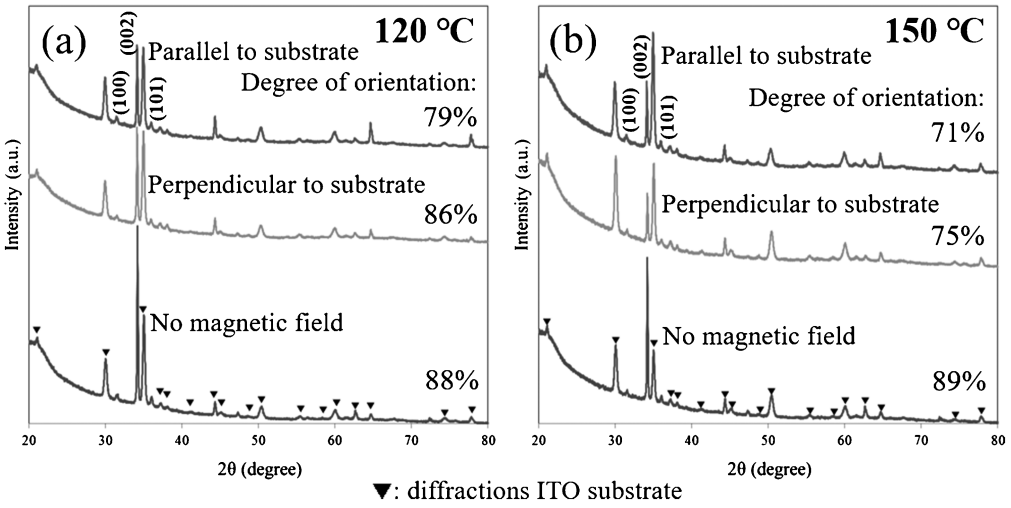

Fig. 8 XRD patterns of nanorods formed on the substrate from zinc hydroxide solution under a magnetic field of 12 T with PEG additive; additive amount: 0.1 g; reaction temperature: (a) 120°C, (b) 150°C. For comparison, XRD pattens for no magnet field are also shown at each temperature.

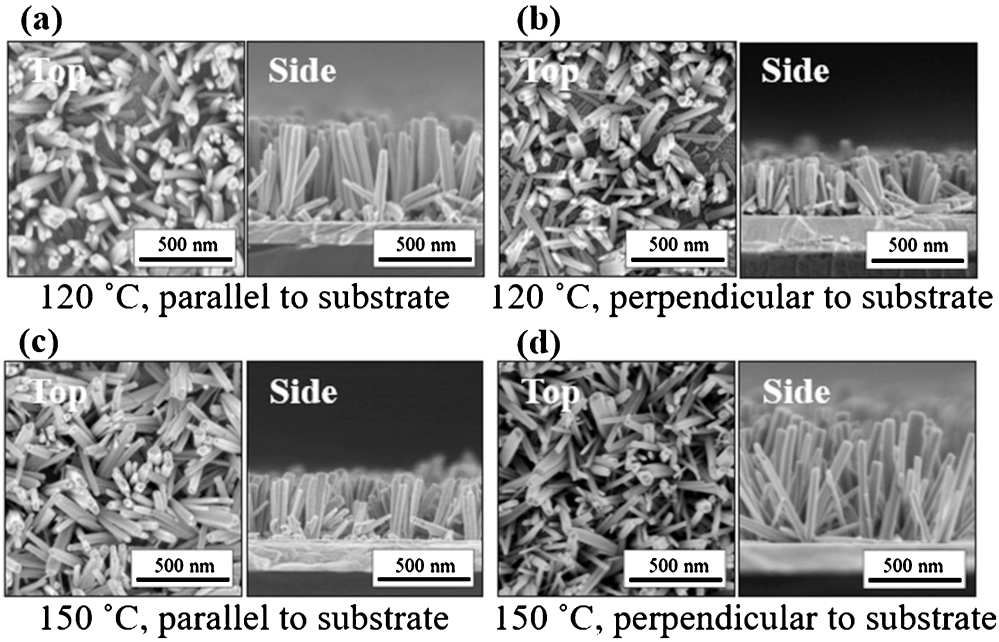

Fig. 9 SEM images of nanorods formed on the substrate from zinc hydroxide solution under a magnetic field of 12 T with PEG additive; additive amount: 0.1 g; reaction temperature: (a), (b) 120°C, (c), (d) 150°C.

cation was significant due to the suppression of convection flow, although as in the case of no magnetic field, the degree of orientation was increased by the addition of PEG.

4 Summary

The hydrothermal synthesis of ZnO nano-sized rods was carried out using a PEG additive and applying a high magnetic field, and the effects on the respective ZnO morphologies were investigated.

For the synthesis of ZnO rod-shaped particles via homogeneous nucleation in a $Zn(OH)_2$ solution, PEG was used as an additive. At pH = 10.3–5, the adsorption of PEG inhibited the growth of the entire particles, resulting in a decrease in both the length and thickness, whereas at pH > 11, the increase in $-Zn-O^-$ on the (0001) surface resulted in preferential adsorption on the side surface of the ZnO hexagonal prism, which promoted c–axis growth, resulting in a significant increase in the particle length. The PEG addition had a similar effect on the growth of the ZnO rods on the substrate. The length and thickness of the rod-like particles increased. The degree of orientation then increased accordingly.

When a strong magnetic field was applied to the hydrothermal synthesis of the ZnO rods on the substrate, convection of the reaction solution was suppressed, resulting in a reduction in the growth rate and orientation. The simultaneous addition of PEG and application of the strong magnetic field did not have the same effect as in the case of PEG addition only. The length of the rod-like ZnO particles decreased in the same way as in the case of the application of the strong magnetic field only. The predominant feature of this study is that the synthesis conditions were appropriately varied, and that the synthesized products were observed and evaluated in detail to a degree not seen in previous reports. The summary of this study is that the influence of complex process factors has been experimentally demonstrated.

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水熱法による酸化亜鉛ナノロッド合成におけるポリエチレングリコール添加および強磁場印加効果

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酸化亜鉛ナノサイズロッドを水熱法により合成し，そのサイズと形態を制御した．ポリエチレングリコール(PEG)を添加剤として用い，表面吸着により粒子成長を制御した．PEG の添加によってロッド状の ZnO 粒子が合成され，その形態は反応溶液の pH によって変化した．pH＝10.3–5 では，PEG を添加して合成したロッド状 ZnO 粒子は PEG が粒子全体に吸着してサイズが小さくなった．pH＞11 では，(0001)面の表面 Zn–O^- の露出濃度が高いため，ZnO 六角柱の側面に PEG が優先的に吸着し，c 軸方向の成長が促進されて，ZnO ロッド状粒子の長さが大きくなった．PEG の添加は，基板上に析出した ZnO ロッドに対しても同様の効果を示した．12 T の強磁場下では，反応溶液の対流が抑制され，ZnO ロッドのサイズが小さくなり，配向性が低下した．PEG を添加しても，強磁場下で対流が抑制された結果，ZnO ロッドのサイズが小さくなり配向性が低下がした．