Effect of the surface of a silicon substrate on the growth of ZnO films by a wet process

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Effects of a silicon substrate on growth of ZnO in a wet chemical process were investigated. ZnO has been fabricated from base solutions composed of $\text{Zn}(\text{NO}_3)_2$, ammonia and polyethylene glycol at low temperatures by a wet chemical process. When a silicone substrate was immersed in the solution, flower-like ZnO was obtained on the substrate from the solution at $\text{pH} = 10.4\text{--}10.9$. In the case without the substrates, $\text{Zn}(\text{OH})_2$ powders were obtained from the solution at $\text{pH} = 10.4\text{--}10.9$ and ZnO powders, which were not like flowers, were obtained from solution at $\text{pH} \leq 7.6$.

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1. Introduction

Zinc oxide (ZnO) is one of the most important functional oxides with its wide band gap (3.37 eV at room temperature) and high exciton binding energy (60 meV). ZnO nanostructures have shown superior properties in nanoscale optoelectronics,¹⁾ solar cell electrodes²⁾ and sensor devices.³⁾ Various ZnO nanostructures including wires,¹⁾ belts,⁴⁾ tubes,⁵⁾ rods⁶⁾ and tetrapods,⁷⁾ have been prepared by different methods such as vapor-phase transport, thermal evaporation and chemical processes.

Among the various ZnO structures, rose-like structures consisting of two-dimensional ZnO nanosheets have shown good photoelectrochemical properties as dye-sensitized solar cells.^{8),9)} Such structures are fabricated by pyrolysis of layered hydroxide zinc acetate ($\text{Zn}_5(\text{OH})_8(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) deposited on conducting glass sheets in a chemical bath, resulting in a micro/nanoporous ZnO film. Due to their large surface area, ZnO films show good photoelectrochemical performance.⁹⁾ ZnO nano-flowers are also produced by ultrasonic pyrolysis of zinc acetate dihydrate aqueous solution and have nanostructures that are very porous and jagged due to their crystalline and optical properties.¹⁰⁾ Polyethylene glycol (PEG) is known to be one of the surfactants and can be used to control morphologies and structures of ZnO.¹¹⁾

On the other hand, ZnO powders shaped with flowers have also been obtained from aqueous precursors with zinc sulfate¹²⁾ or nitrate^{13),14)} at low temperatures. The precursors of zinc nitrate with hexamethylenetetramine (HMT) can be also used to make oriented ZnO films, when the seed layers, which were fabricated from zinc acetate by the sol–gel method, were coated on the substrate.^{15),16)} From preliminary estimations, it was difficult to fabricate homogeneous ZnO films without the seed layer. This might show that the surface of the substrate affects the growth of the ZnO from the precursors.

In this study, the effects of the surface on a silicone substrate on the growth of the ZnO films were investigated from the comparison of productions from precursors with and without a substrate. The productions were fabricated by controlling the pH and composition of the precursors containing PEG.

2. Experimental procedures

Precursor solutions were prepared from 50 ml 0.025–0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd., Osaka) and 1 M ammonia aqueous solution (Kanto Chemical Co., Inc., Tokyo) containing 0–10 mass% PEG (molecular weight (MW): 1000, 6000 (Kanto Chemical Co., Inc., Tokyo) or 9000 (Merck Schuchardt OHG, Hohenbrunn, Germany) g/mol). After stirring for 10 min at room temperature, the solutions were transferred into a glass cylinder and silicon substrates were immersed in them. Next, the solution was placed into a water bath at 70 or 80°C for 0.5–6 h. Finally, the substrate was washed by water to remove excessive particles and was dried by N_2 gas blowing.

In order to investigate the ZnO growth mechanism on the substrate, powders were produced by a similar process but without immersing the substrate. The precursor solutions composed of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ammonia solution and PEG were refluxed for 2 h at 70°C, and precipitates were collected by filtering or centrifugation and washed with deionized water and ethanol twice. The precipitates were then dried at 60°C in air and the powders were obtained.

The morphology of the productions on the substrate and that of the powders were analyzed by scanning electron microscopy (SEM; JEOL Ltd., Tokyo). The crystal structures of the samples were characterized using an X-ray diffractometer (XRD; Bruker AXS K.K., Yokohama) with $\text{Cu K}\alpha$ ($\gamma = 1541.8$ nm) radiation and the θ – 2θ scanning technique. XRD patterns were recorded from $2\theta = 10$ to 70° at 0.01° steps.

3. Results

SEM images of typical productions on the Si substrate are shown in Fig. 1. The productions were obtained from 0.05 M

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Fig. 1. SEM images of productions on silicon substrates from the precursors of (a) pH = 10.1, (b) pH = 10.5 and (c) pH = 10.6. Bars indicate 1 μ m.

Fig. 2. SEM images of productions on silicon substrates immersed for (a) 2 h and (b) 6 h into the precursors of pH = 10.5. Bars indicate 1 μ m.

Zn(NO₃)₂ solution and the ammonia solution with 10 mass% PEG (MW = 9000). The pH of the precursor solution was set at (a) pH = 10.1, (b) pH = 10.5 or (c) pH = 10.8 and the precursor solution was maintained for 2 h at 80°C. The productions in Fig. 1(a) show cocoon-like particles, while those in Figs. 1(b) and (c) are like flowers. A comparison of Figs. 1(b) and (c) shows that the flowers fabricated from the pH = 10.5 solution have more petals and are larger than those from the pH = 10.8 solution. When the pH was further increased, the petals of the productions became sharp and the numbers of petals decreased, and no productions were formed on the substrates at pH values above 11. At pH values below 10.1, the productions on the substrates also decreased. Flower-like productions were obtained only at the pH range from 10.4 to 10.9. On the glass cylinders, a little deposition was observed at the pH range from 10.4 to 10.9.

SEM images of other productions obtained from 0.027 M Zn(NO₃)₂ solutions and the ammonia solution with 0.5 mass% PEG (MW = 1000) are shown in Fig. 2. The substrates were immersed into the precursors of pH = 10.6 for (a) 2 h and (b) 6 h at 70°C. Their morphology is like lotus flowers and is highly similar regardless of immersion time. Even at an immersion time of 0.5 h, the morphology of the productions was consistent. These results indicate that the morphology of these productions depends on the pH of the precursor solution, but does not depend on the immersion time.

Figure 3 shows SEM images of productions prepared from 0.5 M Zn(NO₃)₂ solutions containing 10 mass% PEG with different MW, (b) MW = 1000, (c) 6000 and (d) 9000, at pH = 10.5 for 2 h at 80°C. The production prepared from a solution containing no PEG is shown in Fig. 3(a). The morphologies of the productions were like flowers, and the size of flowers and petals increased with an increase of the MW.

Figure 4 shows SEM images of productions prepared from 0.5 M Zn(NO₃)₂ solutions containing PEG (MW = 9000), (a) 1 mass%, (b) 2 mass%, (c) 5 mass% and (d) 10 mass%, at pH = 10.5 for 2 h at 80°C. All productions were like flowers, in which there were many petals regardless of the concentration of PEG.

Fig. 3. SEM images of productions on silicon substrates from the precursors containing (a) no PEG, (b) PEG with MW = 1000, (c) 6000 and (d) 9000. Bars indicate 1 μ m.

Fig. 4. SEM images of productions on silicon substrates from the precursors containing (a) 1 mass% PEG (MW = 9000), (b) 2 mass%, (c) 5 mass% and (d) 10 mass%. Bars indicate 1 μ m.

These SEM images represent that the concentrations of PEG and the immersion time are not important factors to control the morphologies of the productions, and pH of the solution affected strongly the morphologies of the productions.

Figure 5 shows XRD pattern of the typical flower-like productions as shown in Fig. 2(b). Most of the peaks were identified as ZnO (JCPDS card No. 36-1451), and a peak at $2\theta = 29.6^\circ$ was assigned to NH_4NO_3 (JCPDS card No. 47-0867) which might have remained on the substrate. It was found that the flower-like ZnO were obtained on the substrate at the pH range from 10.4 to 10.9.

Figure 6 shows SEM images of the powders obtained from 0.027M $\text{Zn}(\text{NO}_3)_2$ solutions with different pH values: (a) pH = 7.2, (b) 7.3, (c) 8.5 and (d) 10.6. The morphology of the powders was found to depend on the pH values. When the pH value was low, the obtained productions were particles, as shown in Figs. 6(a) and (b). In the case of pH = 7.2 (Fig. 6(a)), the diameter of the spherical particle was smaller than $1\ \mu\text{m}$. When the pH was 7.3, as shown in Fig. 6(b), cocoon-like productions, about $2\ \mu\text{m}$ in length, were obtained. They were similar to the productions shown in Fig. 1(a), although the pH of the precursor solution differs between Fig. 1(a) and Fig. 6(b). At the higher pH level of 8.5 (Fig. 6(c)), two kinds of productions were observed: small particles with size below $1\ \mu\text{m}$ and large polyhedrons. At pH = 10.6, as shown in Fig. 6(d), most of the productions were large

Fig. 5. XRD pattern of the flower-like productions on a silicon substrate shown in Fig. 2(b). ●: ZnO (JCPDS:36-1451), △: NH_4NO_3 (JCPDS: 47-0867).

Fig. 6. SEM images of powders obtained from solutions of (a) pH = 7.2, (b) pH = 7.3, (c) pH = 8.5 and (d) pH = 10.6. Bars indicate $1\ \mu\text{m}$.

polyhedrons with size of greater than $5\ \mu\text{m}$. The size of the productions increased with increasing pH. The polyhedrons fabricated from the precursors of pH ≥ 8.5 were stable and generally did not change, even if the immersion time was long.

Figure 7 shows SEM images of powders prepared from 0.027M $\text{Zn}(\text{NO}_3)_2$ solutions containing 0.5 mass% PEG with (a) MW = 1000, (b) 6000 and (c) 9000 at pH = 7.3. The morphology of powders were cocoon-like particles when the MW of PEG was 1000 and 6000. The morphology was rods and like flowers in the case of MW = 9000.

Figure 8 shows SEM images of powders prepared from 0.5 M $\text{Zn}(\text{NO}_3)_2$ solutions containing PEG (MW = 1000), (a) 1 mass%, (b) 2 mass%, (c) 5 mass% and (d) 10 mass%, at pH = 7.3. All powders were composed of thin rods with diameter below $1\ \mu\text{m}$

Fig. 7. SEM images of powders obtained from solutions containing 0.5 mass% PEG with (a) MW = 1000, (b) 6000 and (c) 9000. Bars indicate $1\ \mu\text{m}$.

regardless of concentration of PEG and few large particles.

The morphology of powders was affected strongly by the pH of the solutions. XRD patterns of the powders prepared from different pH solutions are shown in Fig. 9. The patterns depended on the pH values, and the powders obtained from the precursors at pH = 7.2 showed peaks assigned to ZnO (JCPDS card No. 36-1451); the productions obtained from the precursors of pH ≤ 7.6 were also identified as ZnO. When the pH values

Fig. 8. SEM images of powders obtained from solutions containing PEG (MW = 1000) (a) 1 mass%, (b) 2 mass%, (c) 5 mass% and (d) 10 mass%. Bars indicate 1 μm .

Fig. 9. XRD patterns of powders obtained from solutions of (a) pH = 7.2, (b) 8.5 and (c) 10.6. ●: ZnO (JCPDS:36-1451), ○: ϵ -Zn(OH)₂ (JCPDS: 38-0385).

were above 8.5, new peaks assigned to ϵ -Zn(OH)₂ (JCPDS card No. 38-0385) appeared and the ratio of peaks identified as ZnO to those identified as ϵ -Zn(OH)₂ decreased. Peaks assigned to ZnO disappeared at pH > 10.6.

On the other hand, the morphologies of powders depended on the MW of the PEG as shown in Fig. 7. XRD patterns of these powders were assigned to ZnO because the pH of the solutions were controlled at pH = 7.3. However, the XRD patterns of powders as shown in Fig. 8 were assigned to ZnO and ϵ -Zn(OH)₂. Note that the XRD patterns change according to the morphology of the powders, suggesting that flower- or cocoon-like small powders are assigned to ZnO and polyhedrons or particles with large sizes are assigned to ϵ -Zn(OH)₂. The polyhedrons or particles with large sizes were fabricated more at 70°C than at 80°C.

From the relationship between the morphology of productions and the pH of the precursors, the morphology of the productions fabricated from the same precursors depended on whether the substrate was used as a reaction field or not, and ZnO powders without the substrate formed from the precursor solution with smaller pH values than productions on the substrate.

4. Discussion

The morphology of the productions from the same precursors depended on whether substrates were used or not. The ZnO formed on the substrates from the precursors of pH = 10.1–10.9, although ϵ -Zn(OH)₂ powders, rather than ZnO powders formed from the same precursors without the substrate.

In the precursor solutions, the ammonia solution generally represents the following equilibrium,

The Zn^{2+} reacts with the ammonia, forming $\text{Zn}(\text{NH}_3)_4^{2+}$,

The reaction between $\text{Zn}(\text{NH}_3)_4^{2+}$ and OH^- is expressed by two kinds of equilibrium,

or

When the Zn concentration is 0.025–0.1M and the pH value is above 8, both $\text{Zn}(\text{OH})_2$ and ZnO are stable in the aqueous solution according to the phase stable diagrams.¹⁷⁾ The Gibbs energy of formation of $\text{Zn}(\text{OH})_2(\text{s})$ and $\text{ZnO}(\text{s})$ is -553.6 and 318.3 kJ/mol.¹⁷⁾ Considering the Gibbs energy of formation, $\text{Zn}(\text{OH})_2$ is more stable than ZnO in the aqueous solution. Thus, $\text{Zn}(\text{OH})_2$ forms in the solution at pH > 8 according to eq. (4), when no substrate is used.

On the other hand, when the pH value of the solution is around 7, solid states are not so stable in aqueous solution¹⁷⁾ and OH^- is less than that in the solution with high pH. The $\text{Zn}(\text{NH}_3)_4^{2+}$ reacts with OH^- and form initial ZnO seed crystals as follows,

and

Reaction (6) for the growth of ZnO occurs gradually because the OH^- and NH_4^+ ion concentrations in the solution are small. The slow reaction seems to cause the fabrication of particles with a very small diameter as shown in Fig. 6(a). When the ammonia concentration increases, the growth of ZnO continues and the particle size becomes large as shown in Fig. 6(b).

When the substrates were used as a reaction field, the growth mechanism differs from that of the powders. The surface of the

substrate undergoes negative changes in the alkaline solution because the ζ -potential of a silicon substrate is negative regardless of the pH value.¹⁸⁾ The surface of the silicon might gather ions with a positive charge such as ZnOH^+ , which are obtained from Reaction (5). The ZnOH^+ ions gathered on the substrate react easily and fabricate ZnO seeds by Reaction (6). The seeds grow rapidly and the flower-like ZnO are fabricated on the substrate at the higher pH values.

The difference in the morphology of the productions indicates that the surface of the substrate plays an important role in the growth of ZnO crystals. Although there are many fabrication techniques for ZnO based on pH control of the chemical solutions,¹⁹⁾ the reaction on the substrate is sufficient and different productions might be formed whether the substrates are used or not. The present study demonstrates the important role of the substrate in the growth of ZnO crystals.

On the other hand, the morphology of the productions depended on the MW of the PEG in the both cases with or without substrates. PEG is known to be a nonionic surfactant with a long chain in aqueous conditions. The Zn^{2+} can link with the oxygen atom in C–O–C chain of PEG, and ZnO would grow along the chain of the PEG.¹⁹⁾ Then, the size of productions depended on the MW of PEG, that is, the size of ZnO flowers increased with an increase of the MW.

5. Conclusions

In summary, ZnO productions were fabricated from zinc nitrate solutions by a wet chemical process at low temperatures. When the solutions were reacted without a substrate, ZnO powders were obtained from the solution at $\text{pH} \leq 7.6$ and ZnO and $\epsilon\text{-Zn(OH)}_2$ powders were obtained at $\text{pH} \geq 8.5$. The flower-like ZnO grew on a silicone substrate from precursor solutions under alkaline conditions from $\text{pH} = 10.1$ to $\text{pH} = 10.9$. The Zn productions affected whether the substrates existed in the precursors or not. The surface fields of the substrate were suitable to form the ZnO seeds at a higher pH range than the aqueous conditions, and the flower-like ZnO was formed. Flower-like ZnO is

expected to be useful in photoelectronic devices such as solar cells due to its large surface area.

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