Selective Homoeipitaxial Growth of ZnO Layers on c(+)-Surface by Solvothermal Reaction in Water–Ethylene Glycol Solvent

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ABSTRACT: Solvothermal deposition of ZnO layers on the c(±)-surfaces of ZnO single crystal substrates in a water–ethylene glycol solvent was investigated. Homoeipitaxial growth of nanoparticularate layers was observed on the c(+)-surface. The manner of nanoparticle deposition on the c(+)−surface was similar to that of spherical particles precipitated in the solution, in that both grew through the oriented attachment of small particles during the early growth stage. The growth of the nanoparticularate film on the c(−)-surface was much slower than that on the c(+)−surface. After aging, the top surface of the film on the c(+)-surface transformed into a layer of pyramid-like particles so that the base of the pyramids was directed toward the surface. In contrast, randomly oriented pyramidal particles covered the c(−)-surface. Ostwald ripening through dissolution–recrystallization transformed the nanoparticles into pyramid-shaped particles in the latter stage when they were in contact with the solution. The faster growth on the c(+)−surface than on the c(−)-surface and the pyramidal shape of the particles with c(+)−basal plane deposited on the c(±)-surfaces after aging confirmed that the growth of the c(+)−plane was promoted, whereas the growth of {1010} and c(−)-planes was inhibited in this solution.

1. INTRODUCTION
Zinc oxide (ZnO) is a electroceramic material that is widely used for varistors, transparent electrodes, phosphors, photocatalysts, and gas sensors because of its wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature. ZnO has a wurtzite-type structure and shows spontaneous electrical polarization along its c-axis. The positive polar face (0001) or c(+)−plane and negative polar face (0001) −c(−)-surfaces are rich in zinc and oxygen atoms, respectively. The polarity is an important feature for ZnO optoelectronic applications. The chemical stability,1,2 catalytic properties,3,4 and electronic properties5,6 are dependent on the polarity. ZnO films have been fabricated by several techniques, such as sputtering,7 chemical vapor deposition (CVD),8 molecular beam epitaxy (MBE),9 pulsed laser deposition,10 and liquid phase epitaxy.11 Solution-based methods are simple and environmentally friendly and can be used for the preparation of complex nanostructures at low temperatures. ZnO films and nanostructures have been synthesized using solution-based methods such as chemical bath deposition,12 hydrothermal deposition,13 electrodeposition,14 spin-spraying,15 and dip-coating.16 Epitaxial techniques are promising for optoelectronic applications. The homoeipitaxial growth of ZnO single crystals and the effect of the substrate polarity have been investigated.7−15 For example, ZnO films grown by CVD were smooth and rough on the c(+)− and c(−)-surfaces, respectively. In the case of MBE, smooth surfaces were obtained on the c(+)− and c(−)-surfaces under different conditions.10,11 Epitaxial growth in solutions is expected to be a simple method. Ehrentraut et al. prepared homoepitaxial ZnO films on a c(+)−surface in aqueous solution.15 They used citrate as a capping agent, which slowed down crystal growth along the c-axis by selective adsorption on the c-planes, and horizontal growth was promoted, as Tian et al. demonstrated in the synthesis of ZnO nanoplates.16

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grew through oriented attachment of small particles in the early growth stage and that the Ostwald ripening process through dissolution–recrystallization occurred, which made the component particles pyramid-shaped in the latter stage. When the solution was agitated during the solvothermal process, dispersed pyramid-shaped particles were obtained rather than spherical aggregates, and they worked as excellent gas sensors. The pyramidal shape, rather than rods or plates, implies that the growth of the $c(-)$-plane and $\{10\bar{1}0\}$-planes is inhibited and that the growth of the $c(+)\text{-plane}$ is promoted in this solution. These results imply homoepitaxial growth on the $c(+)\text{-surface}$ and faster growth on the $c(+)\text{-surface}$ than on the $c(-)$-surface.

In the present study, ZnO growth on the $c(\pm)$-surfaces of ZnO single crystal substrates in a water–EG solvent was examined, and the homoepitaxial growth of ZnO on the $c(+)\text{-surface}$ and $c(+)\text{-plane}$ was demonstrated. The manner of deposition on the $c(+)\text{-}$ and the $c(-)\text{-surfaces}$ was discussed with respect to the precipitation of spherical hierarchical particles or dispersed pyramid-shaped particles.

2. RESULTS AND DISCUSSION

The chemical reactions of zinc acetate and hexamethylenetetramine (HMT) in aqueous solution are as follows:

$$(\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 6\text{HCHO} + 4\text{NH}_3$$

$$\text{NH}_4\text{+} + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{+} + \text{OH}^-$$

$$\text{Zn(CH}_3\text{COO)}_2 \rightarrow \text{Zn}^{2+} + 2\text{CH}_3\text{COO}^-$$

$$\text{Zn}^{2+} + 2\text{OH}^2^- \rightarrow \text{ZnO} + \text{H}_2\text{O}$$

When the aqueous solution is heated, HMT decomposes to formaldehyde and ammonia, which acts as a base and induces ZnO formation.

Figure 1 shows scanning electron microscopy (SEM) images of the cross section and top surface of the ZnO layers deposited on the $c(+)\text{-substrate}$ for different reaction times. At a reaction time of 105 min, a dense particulate layer ca. 400 nm thick was formed (Figure 1a). The size of the particles at the surface and inside the layer was approximately 30 nm. At a reaction time of 70 min, no deposition was observed on either $c(\pm)$-surface. No precipitation occurred in the solution after the reaction for 105 min, which indicates that the particulate layer was formed by heterogeneous nucleation. After a reaction time of 2 h, micron-sized spherical particles were precipitated, as reported in the previous study. The surface of the layer was smooth after the reaction for 105 min, whereas some spherical particles were attached on the surface layer after the reaction for 8 h, as shown in Figure 1b. The thickness of the layer was approximately 2.2 $\mu$m after 8 h reaction time. The layer was composed of particles with diameters of approximately 50 nm (inside the layer). The top-down view shows that the particle size was ca. 100 nm. The cross-sectional view shows that the particles of the top layer had a pyramidal shape with the base of the pyramids directed toward the surface as component particles of the spheres.

Figure 2 shows TEM cross sections of the film deposited on the $c(+)\text{-surface}$ after the reaction for 105 min. The deposited layer was a dense and homogeneous particulate film. The selected-area electron diffraction (SAED) patterns of areas A and B agree with that of area C (i.e., with that of the substrate) and reveal homoepitaxy with oriented aggregation of the crystallites along the $c$-axis. It is evident that the crystal orientation of the particles follows that of the substrate. The SAED spots near the surface (area A) are less sharp than those near the substrate (area B), which implies that the degree of orientation of the particles near the surface was lesser than that of the particles inside the layer, probably due to accumulated disagreement of the oriented deposition. When the homoepitaxial growth can be applied to doped films, it could be a simple method for optical and magnetic devices.
The manner of growth on the c(−)-surface was different from that on the c(+)-surface. Figure 3 shows SEM images of the cross section and surface of the ZnO layers deposited on the c(−)-surface. After the reaction for 105 min, a monolayer of nanoparticles was observed. The size of the nanoparticles was ca. 30 nm, which was the same as those on the c(+) surface, as shown in Figure 1a. The thickness of the c(−)-surface layer (ca. 30 nm) was only 7.5% of that on the c(+) surface (400 nm). After the reaction for 8 h, randomly aligned pyramid-shaped particles with sizes of 50–100 nm were loosely deposited on the initial 60 nm thick nanoparticulate layer. The total thickness of the deposited layer was approximately 700 nm. No precipitation of pyramid-shaped particles was observed in the solution after the reaction for 8 h, which suggests that the deposition of the pyramid-shaped particles on the c(−)-surfaces is induced by the substrate and not by the attachment of pyramid-shaped particles formed in the solution. The deposition of pyramidal particles can be used to improve gas sensing properties because of the high sensitivity of the pyramidal faces. Characterization of the initial layer and its effect on the overlying deposition of pyramid particles requires further study.

Scheme 1a shows a schematic illustration of the time evolution of the ZnO layers deposited on the c(±)-surfaces of ZnO single crystal substrates. On the c(+) surface, aligned deposition of nanoparticles in the early growth stage and sequential growth of the nanoparticulate layer occurred. After the prolonged reaction, the top of the ZnO layer is covered with a base of pyramid-like particles. In contrast, on the c(−)-surface, randomly oriented pyramid-shaped particles are deposited as a thin layer of nanoparticles.

The homoepitaxy on the c(+) surface is similar to that of previously reported spherical particles, as shown in Scheme 1b. In either case, from the early growth stage, crystallites are radially aligned along the c-axis. It is considered that these crystallites grew oriented attachments of small particles on the c(+) surface by sharing a common crystallographic orientation to reduce the surface free energy. Similar oriented growth of attachments has been reported for various inorganic materials, such as TiO$_2$, FeOOH, and ZnO.

It is considered that Brownian motion may allow adjacent particles to rotate to find an low-energy configuration represented by a coherent particle–particle interface. A dipole–dipole interaction would enhance the attachment. In the latter stage of growth, the particles in contact with the solution grow with Ostwald ripening through dissolution–recrystallization in which larger particles grow at the cost of smaller particles, which transforms the component particles into larger pyramidal-shaped crystallites. Only the particles on the surface of the thin film on the c(+) surface show this behavior.

Scheme 1. Schematic Illustration of the Time Evolution of the (a) ZnO Layer Deposited on the c(+) and c(−)-Surfaces of ZnO Single Crystal Substrates, (b) ZnO Spherical Particles, and (c) Dispersed Crystallites

![Scheme 1](https://dx.doi.org/10.1021/acsomega.0c03738)

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surface changed to pyramid-like particles after aging. In the case of spherical particles, all nanoparticles could transform into pyramidal-shaped particles, which may be attributed to cracks caused by aging that enables the solution to penetrate into the spheres. In the case of dense spheres, only the particles at the surface became pyramidal-shaped particles.

The random deposition of pyramid particles on the (−)-surface would be the same as precipitation of pyramid particles under agitation, as shown in Scheme 1c. In both cases, there is no guide to the oriented attachments as with the (+)-surface substrate and the spheres. Ostwald ripening occurs easily and results in a pyramidal shape as the particles are in contact with the solution. The pyramidal crystal shape is specifically attributed to the use of EG because ZnO rods were precipitated in the absence of EG in our previous study and ZnO nanowires grew on the both (±)-surfaces of ZnO single crystals in an aqueous solution of HMT without EG. Both the faster growth on the (+)-surfaces compared to the (−)-surface and the pyramidal shape of the particles deposited on the (±)-surfaces after aging confirm that the growth of the c(-)plane is promoted, whereas the growth of {1010} and c(−)-planes is inhibited in this solution.

3. CONCLUSIONS

We have demonstrated the selective homoepitaxial growth of ZnO layers on (+)-surfaces of single substrates by the solvothermal reaction in a water–EG solvent. A layer of nanoparticles grew homoepitaxially on the (+)-surface with the c-axis alignment from the early growth stage. After aging, the top surface of the film transformed into a layer of pyramid-like particles, so that the base of the pyramids was directed toward the substrate surface. In contrast, the growth on the (−)-surface is slow, and the thickness was 7.5% of that on the (+)-plane at a reaction time of 105 min. After a thin nanoparticulate film is formed in the early growth stage, randomly oriented pyramid-shaped particles cover the substrate in the latter stage.

The manner of the oriented deposition of ZnO nanoparticles on the (+)-surface was similar to that observed for spherical ZnO particles precipitated in the same solution. During the early growth stage, the films and spheres grow through the oriented attachment of small particles by sharing a common crystallographic orientation to reduce the surface free energy. In the latter stage, Ostwald ripening through dissolution–recrystallization transforms the component particles into pyramidal-shaped particles. The random deposition of pyramid particles on the (−)-surface is the same as the formation of particles under agitation. In both cases, there is no guide for oriented attachment as with the (+)-surface substrate and spherical particles, and the particles were in contact with the solution. As faster growth was observed on the (+)-surface than on the (−)-surface and the particles deposited on the (±)-surfaces after aging took on a pyramidal shape, it was confirmed that the growth of the (+)-plane is promoted, whereas the growth of {1010} and c(−)-planes is inhibited in this solution.

4. EXPERIMENTAL SECTION

Zinc acetate anhydride (0.012 mol, Wako Pure Chemical Industries, Ltd.) and HMT (0.012 mol, Wako) were each dissolved in a 20 mL solution of 87.5 vol % EG (Nacalai Tesque, Inc.) and water and then mixed together. Non-miscut ZnO single crystals (10 × 10 × 0.5 mm) with (+)- and (−)-surfaces (Tokyo Denpa Co., Ltd.) were used. The surface of each substrate was polished to a mirror finish; the root-mean-square roughness values for the (+)- and the (−)-surfaces were 0.21 and 0.16 nm, respectively. Each ZnO substrate was placed vertically in the mixed solution in a 50 mL Teflon-lined stainless steel cylindrical chamber with an inner diameter of 44 mm and then heated in an oven at 95 °C for 70 min to 8 h. After cooling, the substrates were washed with ethanol and dried at room temperature.

The cross section and top surface of the ZnO layers were observed using SEM (JEOL, JSM-6500F) and TEM (JEOL, JEM-2100F) with a field emission gun operated at 200 kV and a 160 nm diameter selector aperture. The orientation of crystallites was determined by SAED measurements.

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Notes
The authors declare no competing financial interest.

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