Seed layer morphology influencing on ZnO nanorod growth by hydrothermal synthesis

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Abstract: The structure of seed layers has been considered as a significant factor to dictate the subsequent growth of ZnO nanorods. We carefully studied seed layer structures such as crystallinity, surface crystal orientations, and grain sizes to investigate their effect on ZnO nanorod growth during hydrothermal synthesis. The structure of seed layers was changed by controlling their thickness and further annealing treatments at 200-1000 °C. Among several parameters of seed layer structure, the grain size and the surface crystal orientation were found to make a noticeable change in the morphology of ZnO nanorods. Thick ZnO nanorods were produced on large grains while densely aligned products were observed on the seed layer surface with c-axis orientation. In addition, at the early stage of synthesis, we observed ZnO nanorods with a diameter much smaller comparing to the size of grains consisting of poly- and single crystal. This explains that the nucleation of ZnO crystals start on c-axis oriented domains, and they grow in a length favorably and in diameter gradually, resulting in the formation of ZnO nanorods with the integration of tightly aligned products.

Keywords: Nanostructures; Growth models; Hydrothermal crystal growth; Zinc oxide; thermal treatment

1. INTRODUCTION

Zinc oxide (ZnO) has gained importance in the fields of photonics and electronics owing to its intrinsic properties such as a wide bandgap (~3.37 eV), superior exciton stability at room temperature, transparency in the visible range, and piezoelectricity. Accordingly, ZnO nanostructures are being frequently used in ultraviolet (UV) light emitting diode, piezoelectric transducers, piezoelectric nano-generators, gas sensors, and solar cells.

A vertically-aligned ZnO nanorod array with uniform thickness and length is one of the most significant forms due to easy nanodevice applications. Among several methods to prepare ZnO nanorod arrays, hydrothermal synthesis is attractive as a simple and economical approach with less damage to technologically important substrates such as glass and plastics, and also being suitable for large-scale production.

ZnO nanorods are generally grown on a seed layer that is prepared preliminarily on a substrate utilizing several techniques. Some of the works of such seed-mediated growth suggested that the structures of seed layers strongly affect the quality of ZnO nanorods grown, for instance, orientation, crystallinity, and density. Here, we investigated the effect of ZnO seed layer morphology on ZnO nanorod growth through fabricating nanorods on the seed layers with different thickness and being annealed at different temperature.

2. EXPERIMENTAL

A ZnO seed layer was prepared on a substrate by RF magnetron sputtering. We used a c-plane sapphire as a substrate to produce ZnO nanorods with higher orientation and density, as reported previously. A c-plane sapphire substrate was fixed in the chamber of a RF magnetron sputtering system with a sintered ZnO target (99.99 % purity, High Purity Materials). The distance between the substrate and the target was 50 mm. The chamber was evacuated to a pressure of 5.0 × 10⁻⁴ Pa by a diffusion pump before the generation of plasma. Argon and oxygen at 2.8 sccm and 0.7 sccm (controlled by a gas flow meter) were used as the sputtering gases. After pre-sputtering for 15 min, ZnO thin films were sputter-deposited at room temperature at 1 Pa of the process pressure with RF power corresponding to 100 W. With the different deposition time, the thickness of seed layers was changed from 50 to 150 nm, which were confirmed through a cross-sectional observation by scanning electron microscope (SEM, JEOL JSM-5600). To make a morphological change in seed layers, samples were annealed using an electric furnace under N₂ atmosphere. The structural parameters of seed layers, the crystallinity, roughness, and surface grain size, were measured by atomic force microprobe (AFM, JEOL JSPM-5200TM) and X-ray diffraction (XRD, Rigaku RINT-2100), respectively. The orientation of ZnO crystals at the seed layer surface was measured by electron
backscatter diffraction (EBSD, JEOL).

On the prepared seed layers, ZnO nanorods were grown by hydrothermal synthesis. The seed layer samples were immersed in the mixture of zinc nitrite hexahydrate (0.1 M, 50 mL) and sodium hydrate (1.5 M, 50 mL) solutions. The solution was then heated to 90 °C by an electromagnetic heater to proceed a hydrothermal reaction. After 15 min. (~70 °C), the transparent solution gradually became turbid. The temperature reached to 90 °C after 30 minutes, and the reaction was allowed to proceed for 1.5 h. The white mixture was then cooled down to room temperature naturally. The samples were taken out, sonicated in deionized water, and dried under ambient atmosphere. The samples were also taken out from the solution after 3 and 10 min (30 and 55 °C solution temperatures, respectively) to observe ZnO nanorod growth at the early stage of the synthesis.

3. RESULTS AND DISCUSSIONS

Fig.1(a-f) and (g-l) represent SEM images of ZnO nanorods grown on 50 and 150 nm thick seed layers, respectively. Panels (a) and (g) indicate as-prepared seed layers while panels (b, h), (c, i), (d, j), (e, k), (f, l) correspond to different annealing temperatures, 200, 400, 600, 800, and 1000 °C, respectively. The morphology of ZnO nanorods grown is seen to change according to the thermal annealing of seed layers. In order to investigate the influence of annealing temperature on the diameter and density of nanorods, SEM images of the samples were used to measure their structural parameters.

Figures 2(a, b) show the influence of annealing temperature applied to seed layers with 50 and 150 nm thickness on ZnO nanorods grown, where triangles and circles stand for the diameter and density of nanorods, respectively. ZnO nanorods grown on seed layers with each thickness are observed to exhibit a similar trend according to temperature. By annealing seed layers at 1000 °C, the diameter of ZnO nanorods is seen to increase from 80 to 200 nm. By contrast, ZnO nanorods with less density is observed on seed layers annealed at higher temperature, which is a reasonable change considering the growth of thick ZnO nanorods. It's also worth noting that ZnO nanorods are distributed more densely on seed layers with high-temperature treatment. These morphological changes imply that the nature of seed layers dictates the morphology of ZnO nanorods grown, as suggested in the

Fig.1. SEM images of seed layers with the different thickness and annealed temperature.

Fig.2. Influence of annealing temperature on the density and diameter of ZnO nanorods growth on the seed layers with 50 nm thickness (a) and 150 nm thickness (b).
literature reported previously.\cite{22}

The crystallinity and the surface structure of the all seed layers prepared were examined through XRD analysis and AFM observation, respectively. The crystallinity was evaluated using the full width at half maximum (FWHM) of peaks that are derived from ZnO (002).\cite{23} Based on the AFM images of seed layers, the roughness (Ra) was calculated from:

\[
Ra = \frac{1}{l} \int |f(x)| \, dx
\]

The influence of annealing temperature on FWHM and Ra is shown in Figures 3(a, b), respectively. When higher temperature was applied to seed layers, smaller value of FWHM (blue circles) is seen in both Figs. 3(a, b), indicating that seed layers exhibit higher crystallinity after anneal treatment. This is a well-known phenomenon that atoms recrystallize exploiting the thermal energy given to form highly-crystalline structures.\cite{24,25} On the other hand, the behavior of Ra according to a temperature rise is seen to differ between 50 and 150 nm thick seed layers. The insets (the left in each figure) denote the AFM images of as-prepared seed layers with 50 or 150 nm thickness, which reveal that grains as large as 25 and 45 nm are formed on layers, respectively. With 50 nm thickness, the grains maintain its shape under 600 °C while they transform to bunches at higher temperature (800 °C). This reflects the change in Ra, which is unchanged at temperature less than 600 °C and jump at the range between 600 and 800 °C. In the case of seed layers with 150 nm, the surface roughness is shown in Fig. 3(b) to increase monotonically, being caused by the gradual disappearance of seed grains (see insets in Fig. 3(b)). In concert with the change in the surface structures, a pronounced variation in ZnO nanorod morphology is seen in Fig. 1 and 2 at higher temperature, which stimulates us to focus on the surface crystal direction.

We further investigated seed layers annealed at 600-1000°C where their geometrical transformation appears to emerge clearly. Figures 4(a, b, c) show the EBSD inverse pole figure maps of seed layers annealed at 600, 800, and 1000 °C, respectively. In this observation, the diameter of electron beam used by EBSD is 15 nm, the measured depth correspond to ~10 nm. At the annealing temperature of 600 °C, different crystal faces are found to distribute randomly on the seed layer surface. When higher temperature was applied, almost every crystal is found to display ZnO (0001) crystal orientation as shown in Figs. 4(b, c). Thus, re-crystallization is considered to proceed readily at the outermost surface to orient a crystal plane with the transformation of surface.

Based on the results observed by SEM, XRD, AFM, and EBSD, there are at least two parameters to be considered as playing crucial role in ZnO nanorod growth by a hydrothermal synthesis, those being the grain size and the surface crystal orientation. The proposed growth mechanism is illustrated in Figures 5, where SEM images show surface structures at the growth time corresponding to that in each illustration. Fig. 5(a) depicts ZnO nanorod growth on seed layers containing grains with several sizes. Since the c-axis is well known as the fastest-growing direction.
direction of the hexagonal wurtzite ZnO phase, \[27-31\] Zn\(^{2+}\) and OH\(^-\) in a solution are consumed to form ZnO nanorods on the c-plane oriented surfaces on grains. As seen in a SEM image (The second image in Fig. 5(a)), the diameter of nanorods are around 20 nm, which is much smaller than that of the final products. When the grain size is larger than that of single c-plane domain, several nanorods are grown on one grain, leading to the integration of several ZnO nanorods to be thick products. Meanwhile, the grains composed of few c-plane domains appear to favor the growth of thinner ZnO nanorods. The influence of grain size is believed to be seen as ZnO nanorods grown on seed layers with grains different in size. On 45 nm grains, the diameter of ZnO nanorods is observed to be 90 nm (Fig. 1(g-i)), which is 1.2 times larger than nanorods grown on 25 nm grains (Fig. 1(a-c)).

The second parameter is the crystal orientation of c-axis [0001], which triggers the preferential growth of ZnO nanorods. As mentioned above, the probability of ZnO growth should be higher on a seed layer with c-axis oriented surfaces. By SEM measurements, we confirmed that nuclei are newly formed at the early stage of a growth process (SEM images in Fig. 5(b)), and indeed further growth of ZnO nanorods with higher density. The size of nuclei is 20 nm, which contributes to the growth of thick ZnO nanorods. In addition, since ZnO nanorods are seen to stand tightly, leading an easy formation of joints between nanorods to produce large-diameter nanorods as they grow. It should be noted that the shape of several nanorods are observed to be not a hexagon but a distorted form, which probably results from the random fusion of closely packed nanorods. We have to mention that the crystallinity is excluded here as a main factor that influences ZnO nanorod growth. A comparison between ZnO nanorods grown on seed layers with and without annealing treatment at 200 °C reveals that the crystallinity causes almost no difference in the ZnO morphology.

4. CONCLUSION

In summary, the influence of seed layer structures was studied through ZnO nanorod growth on seed layers with different thickness and being annealed at different temperature. Each seed layer was observed by SEM, XRD, AFM, and EBSD. Seed layers without a thermal treatment were seen in AFM images to be granular surfaces while their size of grains and roughness were different depending on the film thickness. At 50 and 150 nm thickness, the grain size on seed layers were observed to be nanometer size, which are found to provide ZnO nanorods with 70 and 90 nm diameter, respectively. Seed layers thermally-treated at 200-600 °C kept grains with the slightly improved crystallinity. When the higher temperature (800-1000 °C) was applied, seed layer surfaces were transformed to be smooth with c-axis oriented crystals, where the nanorods with a diameter as large as ~200 nm were found to be grown much densely on such films. Based on the above, it was concluded that two parameters, the grain size and the surface crystal orientation, play a crucial role in ZnO nanorod growth. The influence of seed layer morphology on the growth of ZnO nanorods observed in this study is believed to be important for a precise control over the density, diameter, and orientation of the ZnO nanorods.

Acknowledgements

This research was supported by Japan Society for the promotion of Science (No.26390102 and 17K05103). We thank Prof. Masaki Tanemura for SEM and AFM measurement, and Prof. Tadachika Chiba for EBSD measurement.

References

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The diameter of ZnO nanorods is observed to be 90 nm (Fig. 1(g-i)), which is 1.2 times larger than nanorods grown on seed layers thermally-treated at 200-600 °C kept grains with the different thickness and being annealed at different studied through ZnO nanorod growth on seed layers with grains different in size. On 45 nm grains, the size is believed to be seen as ZnO nanorods grown on seed growth of thinner ZnO nanorods. The influence of grain ZnO nanorods to be thick products. Meanwhile, the grains than that of single c-plane domain, several nanorods are on the c-plane oriented surfaces on grains. As seen in a and OH- in a solution are consumed to form ZnO nanorods of nanorods are around 20 nm, which is much smaller than the grain size on seed layers were observed to be nanometer size, which are found to provide ZnO on such films. Based on the above, it was concluded that large as ~200 nm were found to be grown much densely oriented crystals, where the nanorods with a diameter as surfaces were transformed to be smooth with c-axis and orientation of the ZnO nanorods. ZnO nanorods observed in this study is believed to be the surface orientation, play a crucial role in ZnO nanorod growth. two parameters, the grain size and the surface crystal on such films. Based on the above, it was concluded that in summary, the influence of seed layer structures was growth mechanism grown on seed layers reveals that the crystallinity of ZnO nanorods of ZnO nanorods grown on seed layers with AFM, and EBSD. Seed layers without a thermal treatment and orientation of the ZnO nanorods. Promotion of Science (No.26390102 and 17K05103). We thank Prof. Masaki Tanemura for SEM and AFM promotion of Science (No.26390102 and 17K05103). We This research was supported by Japan Society for the 3. CONCLUSION

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(Received November 10, 2017; Accepted September 24, 2018; Published Online December 1, 2018)