Densely aligned ZnO nanoneedle arrays prepared via room temperature growth

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The room temperature growth of ZnO nanoneedle arrays on seed layers was demonstrated via wet-chemical synthesis. The orientation of ZnO nanoneedles was found to be extremely high on the flat seed layer with high crystallinity, whereas a poor orientation was observed on rough seed layers. We expect that the direction of ZnO [0001] (c-axis) dictates the orientation of ZnO nanoneedles. With longer reaction time, ZnO nanoneedles grew dominantly in a length compared to a diameter. Dense ZnO nanoneedles with a high orientation is believed to be promising for many applications in optoelectronics and photonics.

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1. Introduction

The synthesis of diverse nanomaterials has been a basis for the development of advanced and multi-functional devices in various fields.¹⁻⁴ Zinc oxide (ZnO) is one of the most versatile materials owing to wide direct bandgap (3.3 eV) and large excitonic binding energy (60 meV) at room temperature (RT), which is stimulating us to produce many types of ZnO nanostructures for potential applications in optoelectronics and photonics.⁵⁻⁸

The array consisting of ZnO nanorods or nanoneedles is one of the most significant forms due to a large area production and easy device applications, being generally synthesized on a seed layer that is preliminarily prepared on a substrate in a high temperature solution.⁹ The RT synthesis is an attractive approach owing to the stationary environment, which could lead uniform size and shape of products, as well as avoid the attachment of unintended byproducts because of a less convection. In addition, this approach will expand the choice of substrates, allowing the use of technologically important polymer substrates.

To the best of our knowledge, the RT growth of ZnO nanorod and nanoneedle arrays have been reported in just a few.¹⁰⁻¹² ZnO nanorod and nanoneedle arrays were demonstrated to be synthesized by a wet-chemical and an electrochemical method at RT, respectively. In those studies, however, the substrate used was a Zn foil, which restricts a substrate where ZnO is formed. Q. Li and coworkers studied carefully the formation of density- and dimension-controlled ZnO nanorod arrays through a RT solution synthesis method.¹² ZnO nanorods are synthesized on a pre-formed ZnO seed-layer, being applicable to a variety of substrates. Herein, we demonstrated the RT growth of ZnO nanoneedle arrays with an extremely high orientation on well-tailored seed layers.

2. Experiments

Using a RF magnetron sputtering technique, a ZnO seed-layer was formed on a c-plane sapphire substrate, on which ZnO crystals tend to be aligned to c-axis. A substrate was fixed at 50 mm away from a sintered ZnO target (99.99% purity, High Purity Materials) in the chamber of a sputtering system. After the chamber was evacuated to a pressure of less than 1×10⁻⁴ Pa by a diffusion pump, argon and oxygen gases were injected at 2.8 and 0.7 sccm, respectively. A ZnO target was pre-sputtered for 15 min, and then, a seed-layer was formed through the deposition of ZnO onto a substrate at 200°C and 1 Pa of a process pressure with RF power equal to 100 W. To tailor the morphology of seed layers, further anneal treatments were conducted under N₂ atmosphere at different temperatures (400–1000°C) for 1 h.

ZnO nanoneedles were grown on seed layers via wet-chemical synthesis at ~24°C. Seed layers prepared were placed to a downward direction in the mixture of zinc nitrite hexahydrate (0.1 M, 80 mL) and sodium hydrate (1.5 M, 80 mL) solutions. The flask in which seed layers and the solution contained was sealed with aluminum foil and kept under a cool (~24°C) and dry environment for several tens of hours (12–48 h). After the synthesis, the sample was sonicated in deionized water, and finally dried in air. For a control experiment, a ZnO nanorod array was also synthesized by a conventional hydrothermal synthesis. An as-prepared seed layer was immersed in the same solution, and heated at 90°C for 2 h. The sample

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was sonicated in deionized water and dried naturally in air.

The surface morphology and the crystallographic structure of ZnO seed layers were measured by atomic force microscope (AFM, JEOL JSPM-5200TM) and X-ray diffraction (XRD, Rigaku RINT-2100), respectively. In XRD analysis, the size of crystallites was calculated using Scherrer formula.9),13) The morphology of ZnO nanoneedles and nanorods prepared was observed by a scanning electron microscope (SEM, JEOL JSM-5600). In this study, the diameter and length of nanoneedles were defined as the width at the middle and a distance between the top surface of seed layers and the head of nanoneedles, respectively, which were measured by means of SEM.

3. Room temperature growth of ZnO nanoneedles

Figures 1(a) and 1(b) represent the SEM images of ZnO products grown on an as-prepared seed layer via RT growth and hydrothermal synthesis, respectively. The reaction time for RT growth corresponds to 24 h. The product shown in Fig. 1(a) corresponds to the part that shows a better alignment in the sample. It is well seen that the RT synthesis provides thin and sharp-pointed ZnO nanorods compared to those prepared via conventional hydrothermal synthesis. In this study, such sharp nanorods produced are referred to as nanoneedles. The appearance of sharp edges at the top of products is expected to be due to the low surface mobility of adsorbates on products. Under the room temperature condition (~24°C), ZnO molecular species adsorbed at the product surface are not active enough to diffuse to less stable surfaces [polar faces e.g. (0001) and (1011)] at the top of nanorods, which results in the formation of sharpened structures.14)

The elongation of ZnO nanorods is dominant while the diameter is almost stable within the range from 60 to 80 nm. ZnO [0001] is well known as the fastest growing direction,15)17) which results in the preferential growth of nanoneedles in a long axis direction. On the other hand, since ZnO nanoneedles are densely packed together, the synthesis solution is not easy to penetrate to the space between nanoneedles, and therefore, the growth in diameter may be suppressed due to the lack of resources such as Zn2+ and OH−.

4. Variation in the orientation, length, and diameter of ZnO nanoneedles

Figures 3(a)–3(c) show representative SEM images of ZnO nanoneedles grown on seed layers with different morphology. The growth time was 24 h. Figures 3(b)–3(c) indicate different annealing temperatures that were applied to change the morphology of seed layers, 400, 600, 800, and 1000°C, respectively. In Fig. 3, we found a significant variation in the orientation of nanoneedles while diameter and length are also seen to be influenced by the annealing temperature.
To observe the nanoneedle orientations, the angle between ZnO nanoneedles and substrate surface was measured by SEM. Figure 4(a) shows an orientational change with respect to the temperature applied for seed-layer annealing. Here, the orientation is evaluated using the standard deviation of the angle, which is indicated as error bars in Fig. 4(a). This result clearly proves that ZnO nanoneedles are aligned with extremely high orientation, and being almost perpendicular to a substrate on the seed layer annealed at 1000°C. A poor orientation is observed at lower temperature, while a gradual improvement is seen with an increase in the annealing temperature.

Figure 4(b) shows the influence of the annealing temperature on the diameter (blue) and length (red) of ZnO nanoneedles. The diameter of ZnO nanoneedles are seen to increase at the temperature less than 600°C, and is stable at higher temperature. The length of ZnO nanoneedles are seen to increase monotonically with a temperature rise.

The influence of geometrical parameters observed is expected to be derived from the structures of seed layers. AFM images of seed layers with and without an anneal treatment are shown in Figs. 5(a)–5(e). Panel (a) and panels (b–e) stand for seed layers that are as-prepared and annealed, where panels (b–e) denote different temperatures, 400, 600, 800, and 1000°C, respectively. The AFM image of an as-prepared seed layer display grains at the surface, whose size corresponds to 36 nm in average. The grains with the similar size are observed at seed layer surfaces annealed at 400–800°C, and the surface structure is found to transform into larger agglomerates to form a flat surface by 1000°C annealing. It is noted that the 1000°C-annealed seed layer also shows some mounds with grooves on its surface, which induced the large cracks of ZnO nanoneedles, as seen in Fig. 3(e) (the part circled by red dots). By means of those AFM images, the surface roughness of seed layers was evaluated by calculating the root mean square deviation (Rq). Note that, regarding the seed layer heated at 1000°C, the part of deep grooves where no products are seen were excluded for the evaluation. Figure 5(f) shows the relationship between surface roughness and annealing temperature. The value of roughness increased until a certain temperature (600°C), and then decreased with higher annealing temperature. The decrease in the roughness value seems to be along with the improvement of orientation [see Fig. 4(a)]. In this regard, however, the drastic improvement of orientation is observed even with the moderate reduction of roughness, which also suggests that not only the surface roughness but also another factor affects the orientation.

Figure 6(a) shows the XRD patterns of a seed layer with and without annealing. The strong and weak peaks at 34 and 72° correspond to (0002) and (0004) in ZnO, respectively. Those peaks are seen in all the patterns while
the peaks shifted to higher angle by an anneal treatment. This indicates that the ZnO crystals of an as-prepared seed layer are mainly oriented to $c$-axis, and then crystallized due to annealing.\(^{18-20}\) Figure 6(b) shows the relationship among the crystallinity of seed layers, crystallite size, and annealing temperature. The crystallinity was evaluated using the full width at half maximum (FWHM) of peaks that are derived from ZnO (0002) in XRD patterns. At higher annealing temperature, the value of FWHM is seen to decrease gradually. The reduction of FWHM corresponds to an increase in the crystallite size from 25 to 55 nm. Considering the size of grains on seed layers [see Figs. 5(a)–5(e)], the single grains annealed at 400–600 and 800°C are likely to be a polycrystal and a single crystal, respectively. As for the grains heated at 1000°C, their size is larger than 100 nm, which suggests that flat grains consist of polycrystals. Based on correlation between crystallographic and geometrical changes observed, the crystallinity or crystalline size of a seed layer also appears to play a role in the growth of ZnO nanoneedles.

Taking into account that ZnO nanoneedles were observed to be highly-oriented with a remarkable change in the surface roughness of seed layers [see Figs. 4(a) and 5], the direction of $c$-plane at the seed layer surface is expected to dominantly dictate the orientation of ZnO nanoneedles in the RT growth. As mentioned above, the grains consisting of multi-crystals on seed layers annealed at low temperature (<600°C) are observed, which implies that various crystal faces are widespread at the surface of a single grain. Since the $c$-axis is the fastest-growing direction, ZnO nanoneedles are favorably grown on $c$-axis domains on polycrystal grains, resulting that ZnO nanoneedles are grown in several directions along the grain curvature. On the other hand, the seed layer annealed at 1000°C displays the flat surface on large grains mostly, which will lead to an almost perfect orientation. On such flat grains, the nucleation of ZnO was expected to take place at (002) planes randomly, leading the growth of well-aligned ZnO nanoneedles., we propose that the flat seed layer with high crystallinity is a key for the growth of highly oriented one
dimensional nanostructures such as ZnO nanoneedles or nanorods via seed-mediated method. The improvement of orientation is well-seen in the seed layers with comparable surface roughness (400 and 800°C annealed) but with different crystallinity. Higher crystallinity is also considered as another factor affecting the orientation while its contribution will be less.

The crystallinity of a seed layer is considered to be a trigger to vary the diameter and length of ZnO nanoneedles. As seen in Fig. 6, the seed layer annealed at higher temperature comprises large crystallites, which enlarges the ZnO crystalline grown to form thick nanoneedles. ZnO seems to grow faster with a neat arrangement along the highly crystallized grains, as mentioned in the reference 21. Therefore, ZnO nanoneedles grew in both length and diameter on well-crystallized seed-layers. The RT growth of highly-oriented ZnO nanoneedle arrays is believed to be beneficial towards offering flexibility to ZnO nanomaterial based devices with high performance, though the non-thermal treatment such as laser annealing is required to obtain highly crystallized seed layers on a heat sensitive substrate (e.g. polymer).

5. Conclusions

In conclusion, ZnO nanoneedle arrays were grown on seed layers at RT (24°C) via wet-chemical synthesis. ZnO nanoneedles with extremely high orientation were found to be produced on a flat seed layers with high crystallinity while a poor orientation was observed on granular seed layers. The direction of ZnO [0001] on the seed layer surface is considered to play a crucial role in controlling the orientation of ZnO nanoneedles grown. The length of nanoneedles changed from 1 to 5 and 2 μm by controlling reaction time (12–48 h) and the crystallinity of seed layers, respectively. The diameter was found not to be affected much by the crystallinity and reaction time. Highly-oriented ZnO nanoneedle arrays demonstrated in this study are believed to be promising for optoelectronics and photonics applications.

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