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Vertical Growth and Morphology Control of Zinc Oxide Micro Rod

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It was tried to fabricate a template substrate having a 3-dimensional structure with micrometer- size diameter in order to extend the p-n junction area of the compound thin film solar cell. The ZnO micro rod layer, which was grown vertically by using the chemical bath deposition, was successfully fabricated as a hexagonal shape along the c-axis which is the preferred growth orientation. The growth of ZnO rod being adequate for device applications was examined through investigating growth mechanism of ZnO rod and optimizing the photo resist profile so as to remove the undercut which was found in the grown ZnO rod. The growth model and material properties of the 3-dimensional ZnO rod were analyzed through the scanning electron microscope.

Keywords Chemical Bath Deposition; ZnO Rod; Photo Resist; Undercut

Introduction

ZnO(Zinc Oxide) has physical and chemical characteristics proper to be applied to next-generation display industry and information industry and thus it is grabbing attention as a material which has a high value for applications. It has wurtzite structure as a compound semiconductor of II–IV type and has a wide band gap of approximately from 3.2 to 3.4 eV at a normal temperature. Also, ZnO has very large free exciton binding energy of 60 meV which is twice that of GaN, which is generally used for luminous element as a direct band gap semiconductor. Therefore, it can cause luminescence by exciton at a room temperature.

ZnO thin film is an excellent material which has various properties such as optical transparency, high refractive index, and a large piezo-electric constant. Since the material can be applied to a wide range of including transparent electrode, window layer [1] of solar cells, UV detector [2], light emitting diode (LED), and laser diode (LD) [3], a lot of researches using its abovementioned properties, are currently in progress.

Recently, a research is being carried out to maximize the p-n junction area to improve the efficiency of optoelectronic device such as solar cells and LEDs. A good example is growing the ZnO rod vertically to maximize the junction area. So far, the research on ZnO

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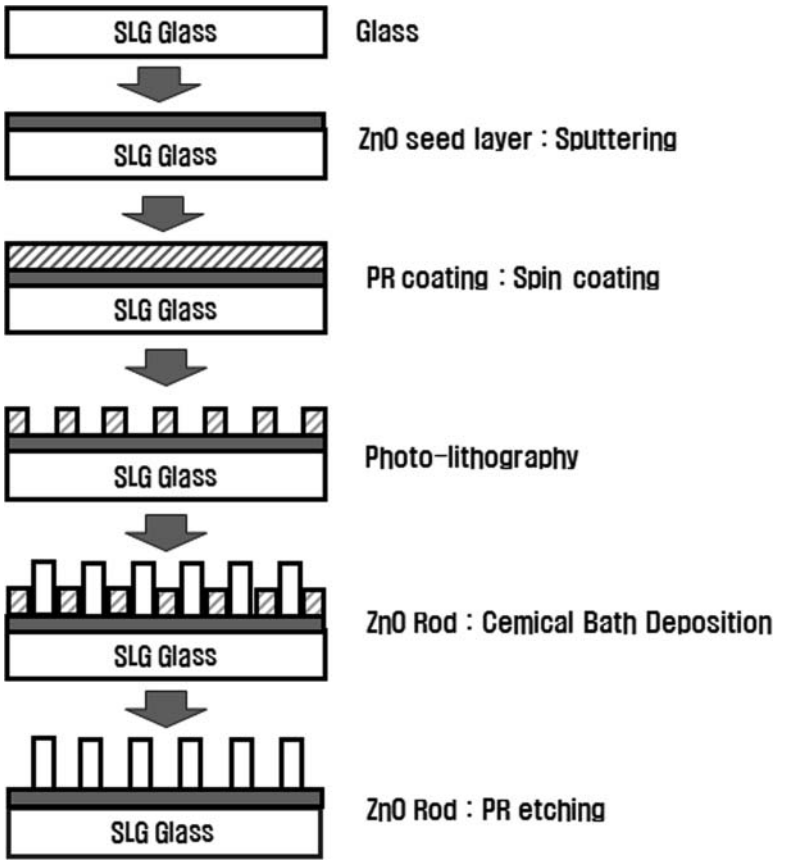

Figure 1. Production process of ZnO micro rod structure.

rod structure has been mostly concentrated on the sensor field using nano-rods. However, nano-sized rods in p-n junction area have limitations to improve the actual p-n junction area.

Using micro-rods instead of nano-rods is favorable for improvement of device performance in terms of extending the p-n junction area. Therefore, in this study, the ZnO rod structure in micro-size was arranged 2 dimensionally and grown vertically in order to develop a device having 3-dimensional junction. The optimized morphology of ZnO micro-rod structure for optoelectronic device was examined by clarifying the mechanism of a complete structure.

Experimental

The experiment was carried out according to the procedure as shown in Fig. 1. First, the 500 nm thick ZnO seed layer was fabricated on the sodalime glass (SLG) substrate using RF magnetron sputtering equipment. The target was 2 wt.% Al doped ZnO with 3 inch diameter and the working pressure and RF power were 3 mTorr and 200 W, respectively. The ZnO rod was grown by using the chemical bath deposition (CBD) process [4].

Also, the size and density of the ZnO rod with 2-dimensional array were adjusted by the photolithographic process. Exposure process was carried out by spin coating of the

photo resist (PR) film on the ZnO seed layer using a mask having the opening of 3 μm diameter and 4 μm spacing. The vertical ZnO rod structure was successfully grown only on the ZnO seed layer opened by the exposure process. Two different kinds of PR such as S1805 (Rohm and Hass, 0.5 μm thickness at 4000 rpm) and S1818 (Rohm and Hass, 1.8 μm thickness at 4000 rpm) were used for the masking process.

Without removing the PR film, the ZnO rod structure was grown using Zinc acetate dehydrate ($Zn(CH_2COO)_2{\cdot}2H_2O$) and HMT ($C_6H_{12}N_4$) as precursors for the CBD process. The reaction used for the CBD is as following [5].

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

$$2OH^- + Zn^{2+} \rightarrow ZnO(s) + H_2O \quad (3)$$

In order to understand the growth behavior of the ZnO micro-rod, the mol concentration of precursors was varied (0.025 M, 0.05 M, 0.075 M and 0.1 M) with a fixed amount of HCl to control the pH at 5.8. In order to avoid the undercut at the bottom of the ZnO micro-rod, the early-stage of the ZnO growth was extensively observed by changing the reaction time, which is counted after adding diluted HCl, from 5 min to 60 min.

The shape and crystalline of the CBD-ZnO micro rod structure and mechanism were analyzed by using the Field Emission Scanning Electron Microscopy (FE-SEM) about two experiments. The optimal structure of the ZnO micro rod for optoelectronic device was expected through the analysis.

Results and Discussion

1. Morphology Characteristics of the Micro-ZnO Rod Structure Grown on Patterned Substrate

Figure 2 shows the SEM images of ZnO micro-rod structures grown on the patterned substrate with various molar concentrations of reactants, 0.025 M, 0.05 M, 0.075 M and 0.1 M with fixed molar ratio of Zn/HMT. Growth characteristics according to the mole concentrations were examined and it was found that ZnO rod was not formed at 0.025 M as shown in Fig. 2(a) and (b), however, under the other conditions of 0.05 M, 0.075 M and 0.1 M, it was found that ZnO rod has been grown vertically with 2-dimensional arrangement.

D. S. Boyle [6] reported that, in the growth of ZnO rod using CBD method, ZnO rod started to grow when the color of the solution turns to milky white 30 minutes after mixing Zn source and HMT of 0.005 M. In this study, in the case of 0.025 M, the reaction was found to be started 25 minutes after mixing the precursors. During the initial delay time of 25 minutes, the reverse reaction in Equation (2), which consumes the OH ions required for the growth of ZnO rod, is believed to happen due to supply of hydrochloric acid. This is why the reaction to form the ZnO rod did not happen for 25 minutes.

As the reaction proceeds, the pH value gradually increases and the forward reaction of Equation (2) occurs to initiate the growth of the ZnO rods. In the case of 0.05 M, 0.075 M and 0.1 M, the reaction was found to be started 12, 6, 3 minutes, respectively, after mixing the precursors. This was a result of the fast process due to the forward reaction of Equation (2), of which the reaction rate is directly proportional to the mol concentration because the effect by hydrochloric acid was relatively smaller than 0.025 M condition. In case of the

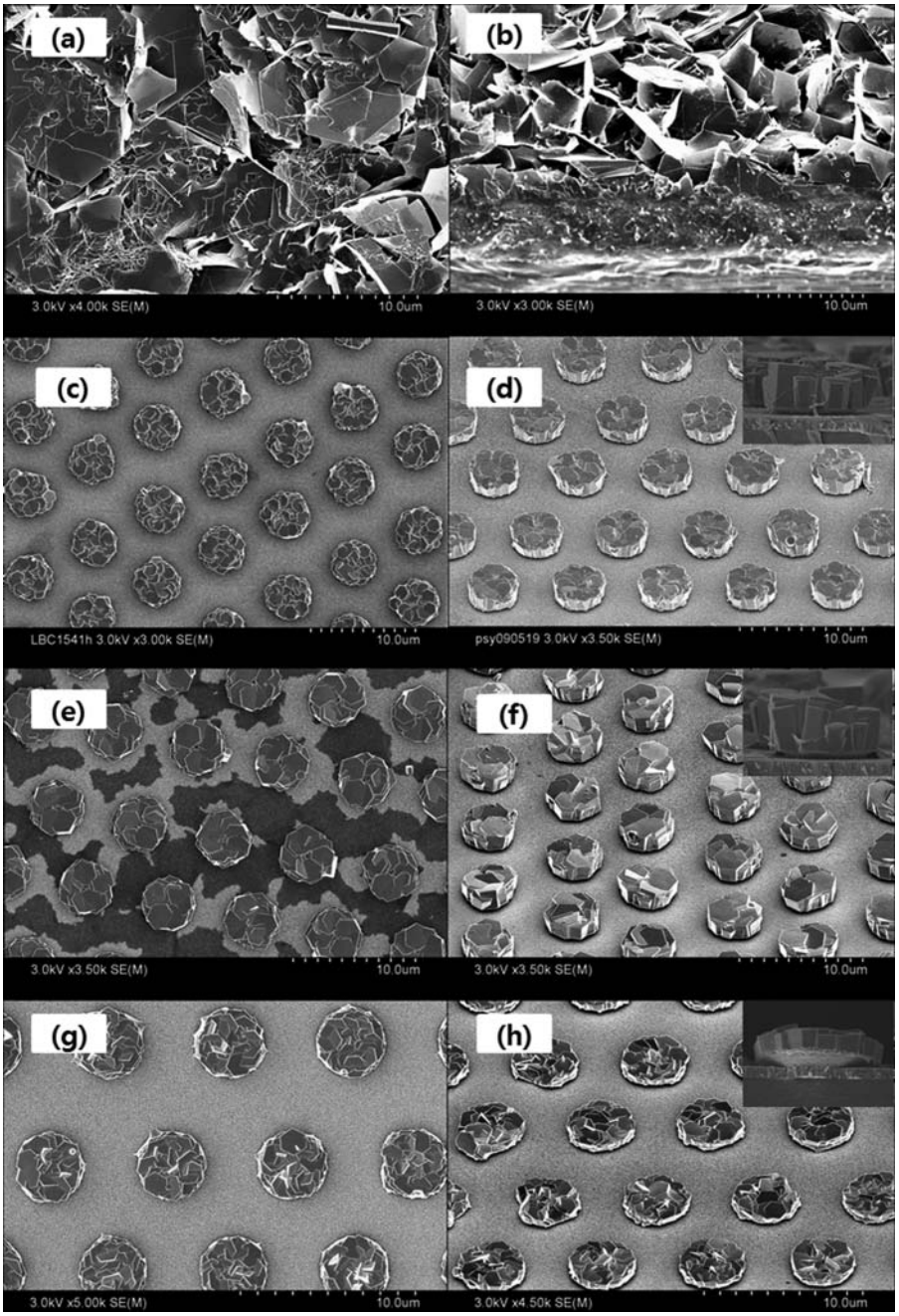

Figure 2. Photos of SEM of ZnO rod according to mol concentration (a, b) 0.025 M, (c, d) 0.05 M, (e, f) 0.075 M, (g, h) 0.1 M.

high concentration of reactant, it was found to be hard to obtain an ideal high aspect ratio for micro-rod morphology.

An excessive undercut makes conformal deposition impossible during the deposition process to form a p-n junction and thus extension of p-n junction area by micro-rod cannot

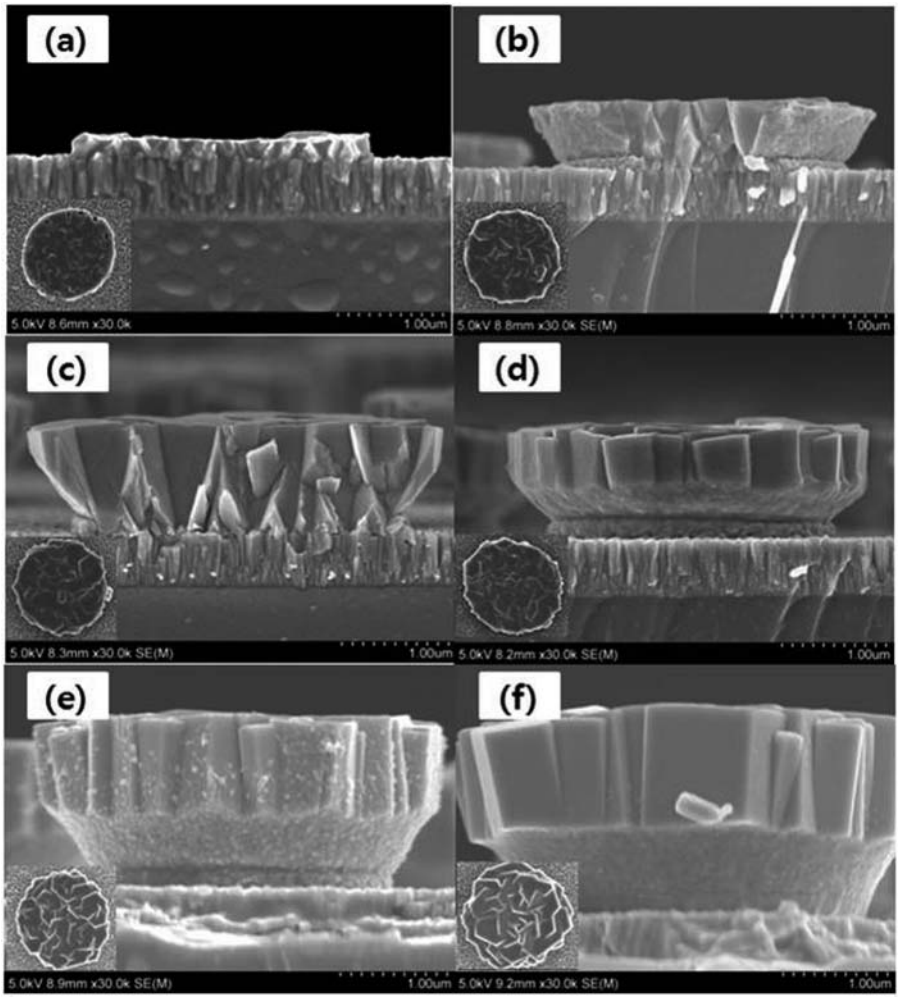

Figure 3. SEM photos of ZnO rod according to reaction time (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, (e) 40 min, (f) 60 min.

be expected. Therefore, besides high aspect ratio, the growth condition without undercut needs to be set. Based on the above comparison of the rod growth behavior depending on the mole concentrations of the precursors, it is suggested that the optimal mole concentrations of the precursor for the rod growth are 0.05 to 0.075 when the initial pH was 5.8.

2. Morphology Characteristics of the Micro-ZnO Rod Structure without Undercut

Figure 3 shows the SEM images of the ZnO rod structure according to the reaction time. It was found that ZnO rod was grown with two stages from beginning with addition of diluted HCI used as pH controller.

In the early stage, the rods grow vertically along c-axis (Figure 3(a)) and to the diameter direction of ZnO rod (Figure 3(b)). Then, only the vertical growth leads the growth of the rod (Figure 3(c)∼3(f)). The two stage growth behavior induces the undercut in the ZnO

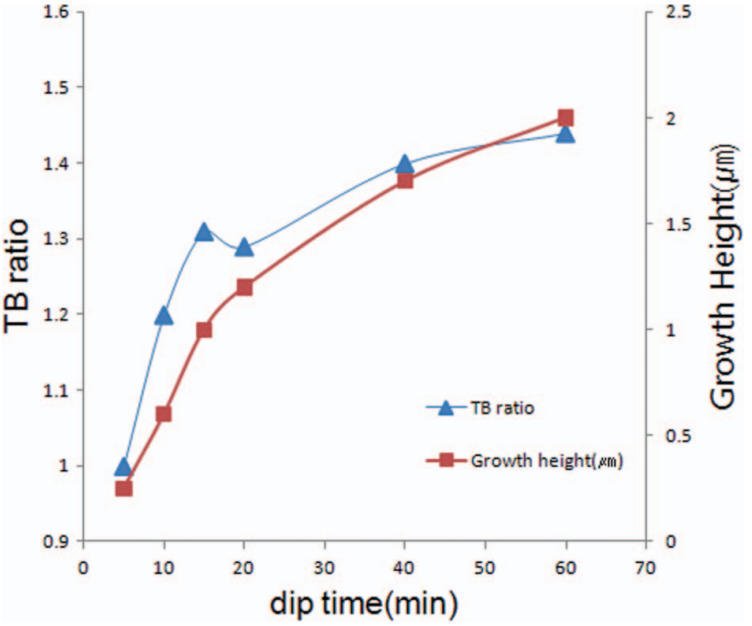

Figure 4. TB ratio and growth height with respect to reaction time.

rod structure. As described before, the undercut must be removed for the continuous p-n junction formation.

The average size of the undercut in Figure 3 was 700 to 800 nm. That is, the undercut is formed by the simultaneous growth of the rods in both of vertical and horizontal directions only when the rod thickness is less than 1 μm.

The ratio of top diameter and bottom diameter of the ZnO rod is defined as TB ratio in order to quantify the growth model and the dimension of the ZnO rod according to the reaction time. Figure 4 shows the TB ratio according to the reaction time. Since ZnO rod grows together both vertically and horizontally in the early reaction, the slope of the early reaction is larger than the following reaction stage. However, as shown in Fig. 3(c), (d), 15 minutes after the reaction, the growth in the diameter direction hardly happens while vertical growth prevails rod growth. That is, in Fig. 4, the slope of TB ratio becomes gentle since the variation of top dimension becomes constant when 15- minute dip time has passed.

Also, it was found that the growth rate of the ZnO rod becomes lower from about 20 minutes. Since relatively a lot of Zn ions exist in the mixture solution during the early reaction time, the rate to form the ZnO rod is high. On the contrary, as shown in Fig. 4, the amount of Zn ions existing in the mixture solution decreased from 20 minutes and thus the slope of the ZnO rod growth became gentle.

If the horizontal growth of the rod could be limited in the early reaction stage, the rod would grow only vertically, which is ideal for the rod geometry with no undercut. Therefore, a thicker PR (S1818, 1.8 μm) was used in the photolithography to make a taller masking over 1μm to restrain horizontal growth of the rod in the early stage.

Figure 5 shows the optimized micro ZnO rod by adopting the thicker PR masking. It is clear that the ZnO rods grow only in the vertical direction to form a 3-dimensional structure without an undercut simply by limiting the early growth mode.

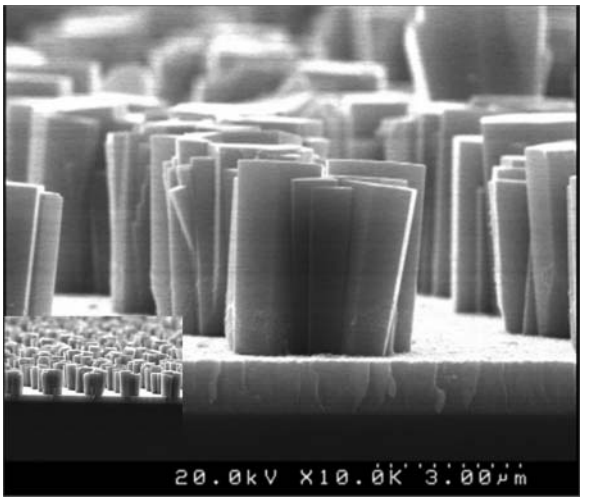

Figure 5. ZnO rod without undercut.

Conclusions

In this study, for optimized growth of the ZnO micro-rod, the precursor mole concentration which functions as a significant variable of chemical bath deposition was set at 0.025, 0.05, 0.075, and 0.1 M as variables. The rod tends to grow in the diameter direction rather than in the vertical direction as the mole concentration becomes higher. By examining the growth behavior depending on the deposition time, it was found that the horizontal growth in the early stage induced the undercut. By increasing the thickness of the photo resist to restrain the horizontal growth of the early stage, an optimized 3-dimensional ZnO micro-rods structure with no undercut which is 3.7 μm in height, 3.7 μm in diameter, with an aspect ratio of 1, was successfully grown.

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