Branches of ZnO nanostructure grown on sub-microrod template with seed layer coated by ultrasonic-assisted immersion technique: effect of surface energy on the growth of branches

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Keywords: hydrothermal, ultrasonic-assisted immersion, ZnO seed layer, hierarchical ZnO nanostructure

Abstract
Branches of ZnO nanostructure were hydrothermally grown on seed layer coated on sub-microrod template by ultrasonic-assisted immersion technique. Zinc acetate, monoethanolamine, and isopropanol were used as a precursor, stabilizer, and solvent for coating seed layer, respectively. The crystallization of seed layer, which was confirmed by x-ray diffractometer (XRD) and x-ray photoelectron spectrometer (XPS), was facilitated by ultrasonic irradiation. The sol concentration was adjusted to be 20 and 50 mM with the coating cycles of 8 and 16 for controlling the uniformity and surface energy of seed layer. The increase of sol concentration and coating cycles led to the increase of crystal orientation in (002) plane causing the improvement of seed layer’s surface energy which was estimated from water contact angle of the template. Atomic force microscope (AFM) was revealed that the seed layer did not cover the template only at the lowest condition of both sol concentration and coating cycles. However, the roughness and maximum peak-to-valley value tended to be increased for other conditions and dropped for the last condition which was suitable to vertically grow branches. After the growth of branches, the morphology of hierarchical ZnO nanostructure was investigated by field-emission scanning electron microscope (FESEM). It was found that the branches were vertically grown on the surface of rod template in every condition except the lowest sol concentration and coating cycles. Moreover, when the sol concentration and coating cycle of seed layer were increased, the branch density was also increased.

1. Introduction

ZnO is one of the most popular semiconducting materials with a wide energy bandgap of 3.37 eV and a large exciton binding energy of 60 meV [1]. Especially, hierarchical ZnO nanostructure has been a useful material with various applications in the field of energy production, such as photoelectrochemical water splitting to produce hydrogen fuel [2] and dye-sensitized solar-cell [3, 4]. To compare with one-dimensional ZnO nanostructure, this structure also has advantages in enhancing the surface area and light trapping properties for using as photocatalyst [5].

Various methods, such as chemical vapor deposition [6], precipitation [7], plant extraction [8], and sol-gel [9], could be used to synthesize ZnO. Hydrothermal is the most common method for synthesis of 1-D ZnO nanostructure because it is low-cost, simple equipment requirement, and environment-friendly [10]. Moreover, it has also been used for the growth of the branched ZnO nanorods on the surface of rod template to produce the hierarchical ZnO nanostructure [2–4, 11–15]. There have been three potential pathways to grow the ZnO branches on template via hydrothermal route: using Zn(OH)\(_2\) solution in the step of the second growth [11, 12], mixing diamine into the second growth solution [13–15], and coating seed layer on the surface of first nanostructures [2–4]. The coating of seed layer is an easy pathway for controlling the morphology of branched ZnO nanostructures comparing with other pathways that grow branches by the mixing of chemical solution.
Previously, sputtering and sol-gel methods were used by many researchers to coat the ZnO seed layer on the surface of the template. The sol-gel method has benefits for the infiltration of particles into nanostructure template [3] comparing with sputtering, which is limited by the shadowing effect.

Ultrasound has been used for creating the acoustic cavitation into solution. The cavitation implosion is localized and transient with a temperature of ~5000 K and pressure of ~1000 bar [16]. Therefore, the ultrasonic wave was used to reduce the reaction time for the crystallization of metal-oxide via the sol-gel method [16–18]. V. Nair et al also reported that a high frequency of collision between nanoparticles on the surface of matter could be produced by ultrasound [19]. Thus, the ultrasonic wave can be applied to coat the seed layer on the surface of the complex template using immersion technique.

There were few researchers that reported about the coating of seed layer on the surface of nanostructures via sol-gel method [2, 3]. X. Ren et al mentioned that the ZnO seed layer with complete coverage was coated on the sub-microrod template by dip-coating technique with a high sol concentration of 750 mM [2]. H.-M. Cheng et al presented that the crystallization of the ZnO seed layer on the nanorod template surface was found by immersion of template into Zn-oxo-acetate solution [3]. However, there has been no report about the influences of seed layer’s surface energy on the growth of ZnO branches.

In this work, ultrasonic-assisted immersion was used for coating of ZnO seed layer on the sub-microrod template produced by an electrodeposition technique. The sol concentration and coating cycle for the coating process were adjusted to control the seed layer’s coverage and surface free energy on the sub-microrod template. The surface energy of seed layer was calculated by the equation of state approach from the seed layer’s water contact angle, which was approximated from the water contact angle of the template with seed layer via Wenzel and Cassie Baxter model. The templates with various conditions of seed layer were used to grow ZnO branches by the hydrothermal method to fabricate the hierarchical ZnO nanostructure. The effects of seed layer’s interfacial energy on the growth of branches were discussed using the classical nucleation theory.

2. Experimental details

2.1. Template preparation

ZnO sub-microrod template was synthesized by an electrodeposition method. Zinc foil (99.9%) and indium tin oxide on glass substrate (ITO/glass; < 10 ohm/square) were used as counter and working electrodes, respectively. Firstly, the electrodes were cleaned by ultrasonic cleaner into acetone, isopropyl alcohol, and DI water. Each of prepared aqueous solutions, such as 10 mM zinc nitrate and 10 mM hexamine, was mixed with volume ratio 1:1 and stirred for 5 min. The mixed solution was used as an electrolyte. Before deposition, the solution was pre-heated for 15 min to reach the deposition temperature at 90 °C. The potential, electrode distance, and deposition time were remained constant at −0.500 V, 2 cm, and 20 min, respectively.

2.2. Coating seed layer on the template

In this process, the mixture consisted of zinc acetate dihydrate, monoethanolamine, and isopropyl alcohol as a precursor, stabilizer, and solvent, respectively. The precursor and stabilizer were used at the same concentration of 20 and 50 mM. To obtain the homogeneous solution, the stirrer was used to mix them for 3 h. In the coating step, the solution and template were put into a laboratory bottle which was stirred for 3 min and sonicated for 2 min in ultrasonic bath with a frequency of 40 kHz and power of 60 W. This step was repeated for 8 and 16 cycles. After coating seed layer on the sub-microrod template, the drying step was introduced to remove the solvent in the ambient condition for 12 h and the samples were annealed at 300 °C in a furnace for 1 h.

2.3. Growing ZnO branches on the seed layer

Aqueous zinc nitrate hexahydrate and sodium hydroxide were prepared separately with concentration of 10 and 40 mM, respectively. Two solutions were mixed with a volume ratio of 1:1 and stirred for 5 min. After preparation of growth solution and template with the seed layer, they were contained into Teflon® liner autoclave which was put into an oven at 90 °C for 6 h to grow the ZnO branches by hydrothermal method. Finally, the template with branches was rinsed with DI water several times and dried by blowing with N₂ gas, respectively.

2.4. Characterization

The morphology of the as-grown template, template with the seed layer, and ZnO branches were investigated by FESEM (Nova NanoSEM 450). The AFM (Park NX-10) was used to characterize the surface topography of the template and seed layer with a non-contact mode. The x-ray diffraction patterns of as-grown template and template with the seed layer were investigated by XRD (Rigaku Smart Lab SE). Further study about oxidation state and elemental composition of the surface of seed layer was performed by XPS (KRATOS AXIS Supra). To
compare ultrasonic-assisted immersion technique with other seed coating techniques, Fourier-transform infrared spectrometer or FTIR (PerkinElmer Spectrum Two) was used to consider the chemical bonding of seed nanoparticles. The water contact angle of the template with the seed layer was measured by a static optical contact angle meter (Kino SL150E) with a drop volume of 2 μl.

3. Results and discussion

3.1. Characterization of seed layer coated on sub-microrod template

The morphology of the template was shown in figure 1(a). ZnO sub-microrod is hexagonal shape, and the surface of the rods is quite smooth, as shown in figure 1(b2). The rods were randomly grown on a substrate with an average rod density ($s$) of 4.64 rod $\mu m^{-2}$. To calculate the surface fraction of sub-microrod surface, the dimension of the rod was measured. Firstly, the average head and base diameters ($D$) of the rods are 256 nm and 443 nm, respectively. Secondly, the average slant height ($L$) of the rods is 1.27 $\mu m$. Thirdly, the head and base edge ($d$) of the rods are 156 nm and 259 nm, respectively. As a feature of the sub-microrod, the surface fraction of the rod surface per total surface area of template was approximated by the following equation:

$$f_{\text{sub-microrod}} = \frac{\text{side surface} + \text{head surface}}{\text{substrate} - \text{base surface} + \text{side surface} + \text{head surface}}$$

$$f_{\text{sub-microrod}} = \frac{3L(d_{\text{head}} + d_{\text{base}}) + \frac{3}{2}(d_{\text{head}}D_{\text{head}})}{1 + 3L(d_{\text{head}} + d_{\text{base}}) + \frac{3}{2}(d_{\text{head}}D_{\text{head}} - d_{\text{base}}D_{\text{base}})}$$

The surface fraction of ITO substrate per total surface area of the template was also approximated by the following equation:

$$f_{\text{ITO}} + f_{\text{sub-microrod}} = 1$$

Therefore, the average value of $f_{\text{sub-microrod}}$ and $f_{\text{ITO}}$ are approximately about 0.974 and 0.026, respectively.

The morphology of the seed nanoparticles coated on the sub-microrod template with different sol concentrations (20 and 50 mM) and coating cycles (8 and 16 cycles) are spherical shape as shown in figure 2. For coating 8 cycles of precursor with 20 mM, seed nanoparticles are sparsely coated onto the surface of the rods as a thin and non-uniform layer, as shown in figure 2(a2). The root mean square of surface roughness ($S_q$) and maximum peak-to-valley value ($S_z$) are 0.4 and 2.2 nm, respectively. When the coating cycle was increased to be 16 cycles, seed nanoparticles could completely cover on the sub-microrod surface with average particle size about 17.8 nm, as shown in figure 2(b2). The $S_q$ and $S_z$ of seed layer at 16 cycles are 0.5 and 2.8 nm, respectively which are close to that of 8 cycles.

When the sol concentration was increased to be 50 mM, seed nanoparticles have more chance to aggregate together that causes increase of average particle size to be 20.2 nm. Moreover, increasing the number of nanoparticles due to increasing the concentration leads to a thicker layer. Thus, at 50 mM and 8 cycles, the $S_q$ and $S_z$ values are 2.7 and 17.3 nm, respectively which are higher than that of seed layer at 20 mM, as shown in figure 2(c2). However, when the number of coating cycle was increased to be 16, seed nanoparticles have more coating duration under the ultrasonic irradiation to fill in the valley area, as shown in figure 2(d2). Therefore, the surface of seed layer is slightly smoother than that of 8 cycles corresponding to a decrease of $S_q$ and $S_z$ values of 1.5 and 10.3 nm, respectively. The average particle size is about 21.4 nm that remains close to 8 cycles.
Figure 3 displays SEM images of ZnO sub-microrods with seed layer. For 20 mM and 8 cycles, the surface of the rods is quite smooth but there are some small straggle fragments of the seed layer. On the other hand, the seed layer at 50 mM and 16 cycles is completely covered on the side surface of sub-microrods that correspond to the morphology of the seed layer investigated by AFM.

The structural property of sub-microrod template with seed layer compared to as-grown template was investigated by XRD and shown in Figure 4. The XRD pattern of the samples corresponds to hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451) and cubic structure of In$_2$O$_3$ (JCPDS card no. 65-3170) from ITO/glass substrate. For the as-grown template, the intensity of (002) peak is higher than that of other planes due to the growth of ZnO sub-microrod in [0001] direction. When the seed nanoparticles coated on the sub-microrod surface, the intensity of (101) peak, which is the highest peak of ZnO powder, would significantly appear.

To consider the quantity of crystallographic orientation in each plane of ZnO, the texture coefficient ($T_{Chkl}$) was calculated using the following equation [20]:

$$T_{Chkl} = \frac{I_{hkl}/I_{0,hkl}}{\sum_{hkl} N_i I_{hkl}/I_{0,hkl}}$$

(3)

Where $I_{hkl}$ is the intensity of (hkl) peak, $I_{0,hkl}$ is the relative intensity of (hkl) peak from JCPDS card, and N is the number of considered peaks. In our case, we used N = 3 that was only three main peaks of ZnO, such as (100), (200), and (101) with relative intensity about 57, 44, and 100, respectively. The results of $T_{Chkl}$ in each sample
were shown in the table 1. The $T_{C002}$ of as-grown template is much higher that of other plane due to the orientation of ZnO nanorod in $[0001]$ direction. When the seed nanoparticles with sol concentration of 20 mM were coated on the sub-microrod surface, the $T_{C002}$ and $T_{C101}$ were dropped and increased, respectively due to presence of ZnO nanoparticles. On the other hand, when the concentration was adjusted to be 50 mM, the $T_{C002}$ was increased because increase of precursor leads to increasing the chance for crystallization of ZnO in highest surface energy (002) plane that causes increasing the size of nanoparticle. Moreover, in cases of both 20 and 50 mM, increasing the coating cycles lead to rising $T_{C101}$ because of increasing the quantity of ZnO nanoparticles.

The template with the seed layer was studied further by XPS. The wide-scan spectra showed the peaks of Zn 2p, O 1s, C 1s, and In 3d, as shown in figure 5(a). The Zn 2p and O 1s peaks could be observed as the main elemental composition of ZnO. The C 1s and In 3d were detected from the acetate group and the ITO/glass substrate, respectively. The oxidation state of the ZnO seed layer was deconvoluted by fitting the Gaussian function, as shown in figures 5(b)–(d). Each spin-orbital peak of Zn 2p was found at $\sim$1021.4 eV and $\sim$1044.4 eV for Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$, respectively. The difference between energy of the two orbital peaks was $\sim$23.0 eV which refers to the Zn$^{2+}$ oxidation state [21]. The O 1s asymmetric peak, which was found at $\sim$530.2 eV, could be fitted from three peaks of different oxygen species, as shown in figures 5(c) and (d). Each peak located at $\sim$530.0, $\sim$531.3, and $\sim$532.3 eV representing the O$_{\text{L}}$ species in the lattice with Zn–O bond (O$_{\text{L}}$), the oxygen vacancy or defects (O$_{\text{V}}$), and the oxygen adsorbed on the surface or OH$^-$ (O$_{\text{A}}$), respectively [22]. When the seed layer condition was adjusted from 20 mM and 8 cycles to be 50 mM and 16 cycles, the intensity of O$_{\text{L}}$ and O$_{\text{V}}$ was increased and decreased, respectively. Moreover, the atomic fraction of the seed layer was calculated from the area under the curves of Zn 2p$_{3/2}$, O 1s, C 1s, and In 3d$_{3/2}$ using the relative sensitivity factor [23], as shown in table 2. The results showed that the atomic ratio of Zn to O was increased from 0.52 to 0.59. These XPS results confirm the improvement of ZnO crystal structure by increasing the sol concentration and coating cycle.

To compare the ultrasonic-assisted immersion with other techniques, including immersion and dip-coating, FTIR was used to investigate the chemical bonding of seed nanoparticles both before and after annealing. The absorption peaks at 2910 and 2970 cm$^{-1}$ were found in all cases, as shown in figure 6(b). They refer to acetate anions originating from the formation of Zn–oxo-acetate nanoparticles during the preparation of

![Figure 4. XRD patterns of sub-microrod template with seed layer coated by ultrasonic-assisted immersion technique with different concentrations and coating cycles.](image-url)

| Condition          | $T_{C002}$ | $T_{C101}$ | $T_{C101}$ |
|--------------------|------------|------------|------------|
| As-grown           | 0.86       | 1.75       | 0.38       |
| 20 mM – 8 cycles   | 0.82       | 1.64       | 0.54       |
| 20 mM – 16 cycles  | 0.80       | 1.52       | 0.68       |
| 50 mM – 8 cycles   | 0.87       | 1.84       | 0.30       |
| 50 mM – 16 cycles  | 0.84       | 1.57       | 0.59       |
Before annealing, in case of dip-coating, the results showed the broad peak at around 3300 cm\(^{-1}\) indicating the N-H and O-H bonds from amine and hydroxyl group, respectively [24] due to accumulation of residue in each coating cycles of zinc hydroxide and amine complex. On the other hand, O-H and N-H peaks were not found in case of immersion and ultrasonic-assisted immersion due to the crystallization of ZnO seed nanoparticles without residue on the sub-microrod surface. However, the residue from dip-coating could be removed by annealing step, as shown in figure 6(b).

The mechanism of coating seed nanoparticle remains unclear. It might be explained by the growth and collapse of acoustic bubbles under the alternative solution pressure induced by an ultrasound wave. While the bubble was collapsing near the substrate, the solution pressure at bubble surface away from the substrate becomes higher than that near the substrate. Thus, solution containing seed nanoparticles penetrated the bubble and rushed onto the substrate that called micro-jetting [19, 25]. As a result, the seed nanoparticles were infiltrated into the template continuously. Moreover, concentrated energy of bubble collapsing could reduce the reaction time for the crystallization of ZnO nanoparticles on the sub-microrod surface [16]. Therefore, from the coating mechanism, an increase of sol concentration leads to the thicker seed layer and larger particle size, and an increase of coating cycle improves uniformity of the seed layer on sub-microrod surface.

### Table 2. Atomic fraction of the template with ZnO seed layer.

| element     | Atomic fraction (%) |
|-------------|---------------------|
|             | 20 mM – 8 cycles    | 50 mM – 16 cycles |
| Zn 2p\(3/2\) | 24.64               | 27.62             |
| O 1s        | 47.72               | 46.56             |
| C 1s        | 20.56               | 19.24             |
| In 3d\(5/2\) | 7.08                | 6.58              |

solution [20, 24]. Before annealing, in case of dip-coating, the results showed the broad peak at around 3300 cm\(^{-1}\) indicating the N-H and O-H bonds from amine and hydroxyl group, respectively [24] due to accumulation of residue in each coating cycles of zinc hydroxide and amine complex. On the other hand, O-H and N-H peaks were not found in case of immersion and ultrasonic-assisted immersion due to the crystallization of ZnO seed nanoparticles without residue on the sub-microrod surface. However, the residue from dip-coating could be removed by annealing step, as shown in figure 6(b).
3.2. Effect of seed layer on the wettability of template

The template with seed nanoparticles was investigated by measuring the water contact angle. While the water drops on the template, it can contact on various surface areas. To understand the wettability of the surface, the combination of Wenzel and Cassie Baxter model could be used to explain by the following equation:

\[
\cos \theta_{\text{exp}} = f_{\text{ITO-W}} \cos \theta_{\text{ITO}} + f_{\text{air}} \cos \theta_{\text{air}} + f_{\text{NP}} \cos \theta_{\text{NP}} + f_{\text{p}} \cos \theta_{\text{p}} + f_{\text{seed}} \cos \theta_{\text{seed}}
\]

Where \( \theta_{\text{exp}}, \theta_{\text{ITO}}, \theta_{\text{air}}, \theta_{\text{NP}}, \theta_{\text{p}}, \text{and} \ \theta_{\text{seed}} \) are water contact angle of template with seed layer, ITO substrate, air, non-polar face of sub-microrod, polar face of sub-microrod, and seed layer, respectively, and \( f_{\text{ITO-W}}, f_{\text{air}}, f_{\text{NP}}, f_{\text{p}}, \text{and} \ f_{\text{seed}} \) are surface fraction (contact with water drop) of ITO substrate, air, non-polar face of sub-microrod, polar face of sub-microrod, and seed layer, respectively. The water contact angles of ITO (\( \theta_{\text{ITO}} \)), air (\( \theta_{\text{air}} \)), and non-polar face (\( \theta_{\text{NP}} \)) are 54.7°, 180°, and 113° [26], respectively.

Because the as-grown template was randomly oriented sub-microrods, the lateral surface has more opportunity to contact with water drop than the vertical surface. Therefore, the water contact angle of as-grown template is around 112° which approaches the \( \theta_{\text{NP}} \), and it means that the wettability of the template is hydrophobic.

Figure 7 shows the water contact angle of template with seed layer (\( \theta_{\text{exp}} \)) coated by ultrasonic-assisted immersion technique with different concentrations and coating cycles. For 20 mM and 8 cycles, the \( \theta_{\text{exp}} \) is around 129° which is a little higher than that of the as-grown template due to higher roughness of the sub-microrod surface by having seed nanoparticles which might trap the air-pockets [27]. In case of 16 cycles, the seed layer could completely cover the rod surface. Therefore, we can ignore \( f_{\text{NP}} \) and \( f_{\text{p}} \) by domination of \( f_{\text{seed}} \) (=\( f_{\text{sub-microrod}} \)) because most of the surface area, which the water drop can be contacted, is seed layer without polar and non-polar surfaces. Moreover, higher surface energy with
random crystal orientation of seed nanoparticles on the non-polar surface helps to improve the penetration of water drop into the template [26] which leads to \( f_{\text{air}} \) close to zero. This means that the \( \theta_{\text{exp}} \) is affected only on the \( \theta_{\text{seed}} \) and dropped to be 106°.

For 50 mM, the \( \theta_{\text{exp}} \) angles for 8 and 16 coating cycles were dramatically decreased to be 39° and 16°, respectively which the wettability of the template are hydrophilic. The decrease of \( \theta_{\text{exp}} \) might be affected by two factors which are the increase of surface energy and roughness coefficient of seed layer. However, we found that the increase of surface areas of seed layer for 8 and 16 cycles are 1.8% and 1.2% which are a little bit higher than that of seed layer at 20 mM and 16 cycles. Thus, the surface energy plays a crucial role in decrease of \( \theta_{\text{exp}} \) due to higher crystal orientation of seed layer in (002) plane.

To calculate the contact angle of the seed layer (\( \theta_{\text{seed}} \)) for 20 mM and 8 cycles, we can approximate \( \theta_{\text{seed}} \) to \( \theta_{\text{exp}} \) because the whole non-polar surface of sub-microrod is not covered by seed layer. On the other hand, when the seed layer could completely cover the sub-microrod surface, the \( \theta_{\text{seed}} \) can be simplified from the equation (4) by substituting \( f_{\text{ITO} - \text{W}} = f_{\text{ITO}}, f_{\text{air}} = 0, f_{\text{NP}} = 0, f_{\varphi} = 0, \) and \( f_{\text{seed}} = f_{\text{sub-microrod}} \), as shown the following equation below:

\[
\theta_{\text{seed}} = \cos^{-1}\left(\frac{1}{f_{\text{sub-microrod}}} (\cos \theta_{\text{exp}} - f_{\text{ITO}} \cos \theta_{\text{ITO}})\right)
\]

The calculated values of the \( \theta_{\text{seed}} \) with different sol concentrations and coating cycles were shown in table 3.

### 3.3. Effect of seed layer’s surface energy on the growth of branches

The surface energy of the seed layer (\( \gamma_{SV} \)) was calculated from \( \theta_{\text{seed}} \) using Kwok and Neumann’s formulation [28]:

\[
\cos \theta_{\text{seed}} = -1 + 2 \sqrt{\frac{\gamma_{SV}}{\gamma_{WV}}} (1 - \beta (\gamma_{SV} - \gamma_{SV}))^2
\]

Where \( \gamma_{WV} \) is the surface tension of water (72.1 mJ m\(^{-2}\)), and \( \beta \) is the parameter in the unit of m\(^2\) m\(^{-1}\). The CAST\(^3\) 3.0 software was used to perform the calculation of \( \gamma_{SV} \). The values of \( \gamma_{SV} \) and \( \gamma_{WV} \) were also used to calculate the interfacial energy between the water and seed layer (\( \gamma_{WS} \)) by Young’s equation

\[
\gamma_{WS} = \gamma_{SV} - \gamma_{WV} \cos \theta_{\text{seed}}
\]

The results show that \( \gamma_{SV} \) increases close to the value of \( \gamma_{WV} \) with decreasing \( \theta_{\text{seed}} \). This leads to the decrease of interfacial energy between the water and seed layer (\( \gamma_{WS} \)) that confirmed the increase of seed layer’s surface wettability and the decrease of \( \theta_{\exp} \). Moreover, the increase of \( \gamma_{SV} \) could influence the morphology of grown branches due to lower energy barrier in the nucleation process.

In previous work, hydrothermal synthesis using the mixed solutions of Zn(NO\(_3\))\(_2\) and NaOH could perform the growth of ZnO nanostructure with high uniformity and rod density [29, 30]. The solution was used to grow the ZnO branches on the template with seed layer, as shown in figure 8. The mechanism for growing branches was described from the chemical reactions below [29–31]:

\[
\text{Zn(NO}_3\text{)}_2 \xrightarrow{25 \degree C} \text{Zn}^{2+} + 2\text{NO}_3^{-2−} \quad (7)
\]
NaOH $\xrightarrow{25 \degree C} \text{Na}^+ + \text{OH}^-$ \hspace{2cm} (8)

$\text{Zn}^{2+} + 2\text{OH}^- \xrightarrow{25 \degree C} \text{ZnO} + \text{H}_2\text{O}$ \hspace{2cm} (9)

$\text{Zn}^{2+} + 4\text{OH}^- \xrightarrow{25 \degree C} \text{Zn(OH)}_4^{2-} \xrightarrow{25 - 90 \degree C} \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^-$ \hspace{2cm} (10)

Zn(NO$_3$)$_2$ and NaOH were dissolved at room temperature (reaction 7 and 8). Most zinc and hydroxide ions would then produce ZnO nuclei (reaction 9). The ZnO branches depending on Zn(OH)$_4^{2-}$ were finally grown on ZnO nucleation layer (reaction 10) in preferred [0001] direction. However, the results show that the uniformity and density of grown branches are different from the previous work due to the coverage and surface energy of seed layer.

The morphology of the branches was short nanorods with a length of 80-110 nm, as shown in figure 8. For sol concentration of 20 mM and 8 coating cycles, the branches with an average diameter of 35 nm were sparsely and mostly lied on the sub-microrod surface, as shown in figure 8(a). This might be due to the thin and non-uniform seed layer leading to the horizontal growth of ZnO. When the number of coating cycle was increased to be 16, the seed layer could cover on the rod surface and was thicker layer. The seed nanoparticles might be developed on other particles in preferred (002) plane due to energetically more favorable interaction between particle and particle [32]. This leads to the vertical growth of branches on seed nanoparticles, as shown in figure 8(b). The average diameter was increased to be 53 nm due to lower branch density.

When the concentration was increased to be 50 mM in case of 8 coating cycles, it caused that the seed layer has more crystal orientation in (002) plane leading to higher number of vertical branches compared to that of branches on seed layer with 20 mM, as shown in figures 8(c) and 9. However, the seed layer still has some thin areas which tend to have lower surface energy due to the lack of (002) orientation leading to lower density of branches, but it can be improved by increasing coating cycle to be 16. The average diameters of branches fabricated with 8 and 16 coating cycles are 43 and 38 nm, respectively.

The relationship between the branch density and surface energy of seed layer ($\gamma_{SV}$) could be confirmed using classical nucleation theory. In case of heterogeneous nucleation, the energy barrier ($\Delta G_{het}^*$) is given by the equation below [33]:

$$\Delta G_{het}^* = \Delta G_{hom}^* \cdot g(\alpha)$$ \hspace{2cm} (11)

Where $\Delta G_{hom}^*$ is the energy barrier in case of homogeneous nucleation, and $g(\alpha)$ is the geometric factor as a function of nucleus contact angle on seed layer ($\alpha$) as shown in the equation below [33]:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{(a) – (d) SEM micrographs and (e) diameter distribution of ZnO branches with different concentrations and coating cycles of seed layer: (a) 20 mM – 8 cycles, (b) 20 mM – 16 cycles, (c) 50 mM – 8 cycles and (d) 50 mM – 16 cycles.}
\end{figure}
The value of \(a \cos \) can be calculated using Young’s equation:

\[
g(\alpha) = \frac{1}{4} (1 - \cos \alpha)^2 (2 + \cos \alpha)
\]

The value of \(\cos \alpha\) can be calculated using Young’s equation:

\[
\cos \alpha = \frac{\gamma_{LS} - \gamma_{NS}}{\gamma_{LN}}
\]

Where \(\gamma_{LN}\), \(\gamma_{LS}\), and \(\gamma_{NS}\) are the interfacial energy between the supersaturated liquid and the nucleus, between the supersaturated liquid and the seed layer, and between the nucleus and the seed layer, as shown in figure 10(a).

We deduce that the \(\gamma_{LN}\) and \(\gamma_{LS}\) are approximately equal to interfacial energy between the water and the seed layer (\(\gamma_{WS}\)) and between the water and the nucleus (\(\gamma_{WN}\)), respectively because the solvent of supersaturated liquid is water as shown in figure 10(a). The \(\gamma_{NS}\) and \(\gamma_{WN}\) were estimated by Dupré’s formula and Berthelot’s combining rule [28] as given by the equations below:

\[
\gamma_{NS} = \gamma_{Z-(0001)} + \gamma_{SV} - 2\sqrt{\gamma_{Z-(0001)}\gamma_{SV}}
\]

\[
\gamma_{WN} = \gamma_{WV} + \gamma_{ZNP} - 2\sqrt{\gamma_{WV}\gamma_{ZNP}}
\]

Where \(\gamma_{Z-(0001)}\) is the ZnO surface energy in (0001) plane (960 mJ m\(^{-2}\) [34]) and \(\gamma_{ZNP}\) is the surface energy of hydrate ZnO nanoparticle (1420 mJ m\(^{-2}\) [35]). Therefore, \(\gamma_{WN}\) is equal 852.2 mJ m\(^{-2}\), and the estimated values of \(\gamma_{NS}\), \(\gamma_{WN}\), \(\gamma_{WS}\), \(\gamma_{NS}\), nucleus contact angle \(\alpha\), and geometric factor \(g(\alpha)\) with different seed layer conditions were shown in table 4.

When the surface energy of seed layer (\(\gamma_{SV}\)) was decreased, it affected the increase of \(\gamma_{WN} - \gamma_{NS}\) leading to the decrease of nucleus contact angle \(\alpha\). This affected the decrease of geometric factor \(g(\alpha)\) which linearly related to the \(\Delta G_{n}^{\circ}\) (equation 11). The nucleation rate (\(J\)), a change of nucleus number per unit time, related to
the $\Delta G_{\text{het}}^*$ that could be given by Arrhenius reaction velocity equation [33, 36]:

$$J = A \exp \left( \frac{\Delta G_{\text{het}}^*}{k_B T} \right)$$  \hspace{1cm} (16)

Where $A$ is the kinetic pre-factor, $k_B$ is the Boltzmann constant, and $T$ is temperature. Since the branch density is linearly proportional to nucleation rate ($J$), therefore, it decreases exponentially with increasing the geometric factor, as shown in figure 10(b). However, for the condition of 20 mM and 8 cycles, the branch density did not follow the trend because the seed layer was thin and non-uniform leading to the growth of branches along the rod surface.

4. Conclusion

ZnO seed layer could be coated on sub-microrod template using ultrasonic-assisted immersion technique. The crystallization of seed nanoparticles on the surface of the rods was confirmed by XRD, XPS, and FTIR. Moreover, the surface coverage and (002) orientation of seed layer controlled by the sol concentration and coating cycles affected the water contact angle of template which related to the surface energy of seed layer calculated by simplified Wenzel and Cassie Baxter model and Kwok and Neamann’s formulation. ZnO branches were successfully grown on the rod surface with seed layer using hydrothermal method. The growing direction of branches was influenced by the uniformity of the seed layer. Moreover, the geometric factor was calculated using the surface energy of seed layer and estimated values of interfacial energy to confirm the variation of branch density through the classical nucleation theory.

Acknowledgments

This research was financially supported by Department of Physics, Faculty of Science, King Mongkut’s University of Technology Thonburi (KMUTT) and by Science Achievement Scholarship of Thailand (SAST). We would like to thank the Central Research Laboratory at KMUTT for supporting the instruments, including AFM and static optical contact angle meter.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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