The effects of precursor concentration and thermal annealing on the growth of zinc oxide nanostructures grown on silicon substrate

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Abstract. This study focuses on the growth of Zinc Oxide (ZnO) nanostructures on SiO2/Si(100) substrate via chemical bath deposition (CBD) with varying NH4OH concentration and annealing temperature. The grown ZnO nanostructures were characterized via SEM-EDS for the surface morphology and elemental composition and UV-Vis spectroscopy for the reflectance measurement. Increasing the concentration of NH4OH produced denser ZnO nanostructures composed of rods having smaller diameter. It is believed that at higher concentration of NH4OH, more Zn(OH)2 seed will act as nucleation site for ZnO formation which suggests higher probability of ZnO growth. Thermal annealing increased the average diameter of ZnO nanorods. Annealing provided enough energy for unstable atoms to rearrange into a more suitable position. This would result to larger rods that have been formed in expense of the smaller rods. Furthermore, it is confirmed in the UV-Vis spectroscopy results that ZnO nanostructures were successfully grown on SiO2/Si(100) substrate. This successful growth of ZnO nanostructures is a promising material for solar cell technology.

1. Introduction

Man’s continuous search for the advancement of science and technology has brought about the production of materials in the nanometer scale. These miniaturized materials have paved the way for significant enhancements in various fields such as biology and medicine, agriculture and business and the electronics industry. In the electronics industry, nanomaterial addressed tremendous issues such as increasing the capabilities of electronic devices while reducing their weight and power consumption. Nanostructured materials possess enhanced optical and photoluminescence properties that are not present in their bulk counterpart.

Among the renowned semiconductor in the research industry is zinc oxide (ZnO). It has received considerable attention owing to its capability to be formed into various morphologies such as nanowires[1] and nanorods[2]. It is a wurtzite-type II-VI compound semiconductor with a relatively large band gap of 3.37 eV at room temperature (RT) [3] and has a large exciton binding energy of approximately 60meV[4] which makes it suitable for wide range of electronic and optoelectronic

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device applications such as light emitting diodes [5] and lasers [6]. Besides, its high electron mobility and high thermal conductivity are also two attributes of ZnO that adds to its promising applications in the semiconductor industry [7].

The crystal quality of ZnO nanostructures is highly dependent on the growth conditions, the growth techniques and the substrates used [8]. For instance, Mitra and Khan [9] reported that growth rate and quality of the ZnO film produced were found to be sensitive to the pH of the zinicate bath. Moreover, Kim et al. [10] found out that the large lattice mismatch (40.1%) and large difference in the thermal coefficients between ZnO film and Si substrate [8,11] will result in the introduction of dislocations and built-in residual stress on the deposited film. However, the unparalleled dominance of Si in the semiconductor industry and the potentials of ZnO as a semiconductor paved the way to the fabrication of ZnO on Si(100) substrate. To address this problem, we utilized amorphous SiO2 to act as buffer layer between ZnO and Si.

In this study, ZnO nanostructures were deposited on SiO2/Si(100) substrates through chemical bath deposition. As mentioned earlier, the large lattice mismatch and large difference in thermal expansion coefficients between ZnO film and Si substrate would cause unfavorable defects. This inherent problem of direct growth of ZnO on Si substrate can be solved by introducing an amorphous SiO2 buffer layer. This SiO2 layer, which is readily incorporated on the Si substrate, will serve as a buffer wherein ZnO particles can easily relax during the growth, thus reducing the strain on ZnO/Si interface and avoiding the introduction of interfacial dislocation. Thermal annealing of the grown samples is carried out to eradicate the impurities incorporated during deposition. The reflectance measurement of the samples is measured using UV-Vis spectroscopy and the surface morphology is examined by scanning electron microscopy-energy dispersive x-rayspectroscopy (SEM-EDX).

2. Experimental procedures
In this study, the substrate used is SiO2/Si(100). The 4-μm thick SiO2 layer is readily incorporated in the Si(100) substrate. The pre-treatment of the substrate strongly affects the deposition of ZnO. The SiO2/Si(100) were first cut accordingly into its desired size. The substrates are then cleaned in distilled water, acetone and ethanol. Zinc oxide were deposited by chemical bath deposition. ZnO growth was carried out by suspending the SiO2/Si(100) substrate in an aqueous solution of zinc sulphate heptahydrate (ZnSO4·7H2O) and ammonium hydroxide (NH4OH). The concentration of NH4OH was varied to two concentrations (2M and 3 M). First, 60mL of zinc acetate solution and 60mL of NH4OH solution were mixed in a beaker. The mixture is stirred at 360 rpm for 30 minutes. Immediately after stirring, the pH of the bath is determined using digital pH meter. The pH is controlled by dropwise addition of HCl to the bath. The cleaned substrates were immersed vertically inside the bath using improvised holders made of glass. Heat is then applied to the ammonium zinicate bath and the temperature is maintained at 70°C by keeping it inside a water bath. When the bath temperature reaches to 70°C, the deposition of ZnO in the substrates will start. The deposition time is 5 hours of constant stirring and application of heat. Using distilled water, the removed substrates are washed and then dried in air for at least 2 hours. Samples are annealed in a furnace at 400° to improve the crystallinity.

3. Results and discussion
This chapter presents the results and discussion of the experiments. Thorough discussions on the growth mechanisms of the synthesized samples, their surface morphology and elemental composition as well as their optical properties are elucidated in this chapter.

3.1. NH4OH concentration dependence
To know the effect of NH4OH concentration of the deposited structures ontoSiO2/Si(100) substrate, the concentration of NH4OH in the solution was varied while controlling the pH of the zinicate bath. Figure 1 shows the SEM images of ZnO prepared from 2M and 3M NH4OH concentration at different magnification. Figure 1 (a) shows lesser density of ZnO nanostructures grown on the surface of the
substrate. Higher magnification is shown in the inset photo. It is observed that the deposited ZnO nanostructures exhibit individual rod-like formation of the nanostructures with scattered sea-urchin-like structures. The sizes of these structures vary from 3 to 10μm. It is observed that a single sea-urchin-like structure is composed of several numbers of nanorods. Each nanorod has well-defined hexagonal surfaces which is a characteristic of ZnO. The average diameter of ZnO nanorods is measured to be approximately 510nm with corresponding length ranging from 3 to 5μm. It can be noticed that smaller urchin-like structures accumulate on top of the larger ones.

Meanwhile, higher concentration of about 3M NH₄OH has been prepared to grow ZnO nanostructures. Figure 1 (b) depicts the SEM images of ZnO sample obtained from 3M NH₄OH concentration at various magnifications. It is observed that the presence of sea-urchin-like structure is very apparent. Denser ZnO nanostructures are obtained for this concentration. It is noticed that more numbers of sea urchin-like structures are found while lesser numbers of individual rods are present. The sizes of the sea urchin-like structures vary from 3 to 8μm. It is noticed that appreciable amount of flakes covered the nanorod structures (not shown). These flakes are believed to be impurities which could be eliminated via thermal annealing. It is clearly shown in the inset photo that the sea urchin-like structures consist of nanorods with an average diameter of approximately 470nm which is smaller compared to the rods obtained using 2M NH₄OH concentration. All nanorods exhibit hexagonal cross section.

Figure 1. SEM micrographs of ZnO grown on SiO₂/Si(100) substrate from 0.03M ZnSO₄ and (a) 2M NH₄OH and (b) 3M NH₄OH with controlled zincate bath pH (11.2) at lower magnification and higher magnification (inset).

For 2M NH₄OH concentration, there are two possible ways in which ZnO will form as shown in the illustration presented in Figure 2. It is suggested that ion-by-ion growth might occur wherein ZnO will be formed through subsequent ionic reaction. The second growth process is the hydroxide cluster mechanism in which Zn(OH)₂ will adhere into the substrate and will attract ZnO forming sea-urchin-like structure. In this concentration, individual rod formations and sea urchin-like structures co-exist as observed in the SEM images. During the addition of the ammonium zincate solution, Zn(OH)₂ precipitation could possibly reoccur leading to sea urchin-like structure formations. The presence of the small sea urchin-like structures that accumulate on top of the larger ones can be explained by the addition of ammonium-zincate solution after 3 hours.
Figure 2. Growth mechanism of ZnO formation for bath with 2M NH₄OH concentration: (a) initial precipitation of Zn(OH)₂ ions in the solution, (b) Zn(OH)₂ adheres into the substrate and individual rod formation, (c) sea urchin-like formation with the nanorods and (d) accumulation of smaller sea urchin-like structure on top of the larger ones.

Meanwhile, for 3M NH₄OH concentration, more Zn(OH)₂ clusters are precipitated in the solution. Schematic illustration of the growth is presented in Figure 3. It is believed that some clusters will adhere into the substrate while other clusters will dissociate to form Zn²⁺ and O²⁻ ions. Zn(OH)₂ clusters adhering into the substrate will attract ZnO atoms forming ZnO nanorods. Since large amounts of Zn(OH)₂ are attracting ZnO atoms, it will be distributed densely into the substrate. As a consequence, smaller rods will be formed. Again, the addition of the second solution after 3 hours might have caused the accumulation of smaller sea-urchin like structures over the larger nanostructures.

Different areas of the grown ZnO samples were considered and measured using EDS, i.e., an area with sea urchin-like structures and an area with no sea urchin-like structures. The EDS result reveals that the sea urchin-like structures are composed mainly of Zn and O which verifies that the produced samples are most likely ZnO. However, the area with no sea urchin-like structures has high peaks of Si and O. This can be explained by the presence of voids in the surface.

Figure 4 shows the reflectance of the samples measured through UV-Vis spectroscopy. Identical curves and peaks were observed for both concentration of NH₄OH with significant variation in the values of the reflectance between 200 to 400 nm. ZnO obtained from 3M NH₄OH concentration (labeled ZnO 3M) has lesser reflectance compared to ZnO sample obtained from 2M NH₄OH concentration (labeled ZnO 2M). Quantitatively, the intensity of the reflectance between 200 to 247.5 nm reduces by about 5% and lessen to 3% in the 247.5 to 300 nm range. However, at 300 to 380 nm, only 2% reduction can be observed. The decrease in the intensity of reflectance might be due to large amount of ZnO deposited unto the substrate at higher NH₄OH concentration which verifies that ZnO 3M is denser compared to ZnO 2M.
Figure 3. Growth mechanism of ZnO formation for bath with 3M NH₄OH concentration: (a) initial precipitation of Zn(OH)₂ ions in the solution, (b) Zn(OH)₂ adheres into the substrate and generation of free radicals into the solution, (c) sea urchin-like structure formation and (d) accumulation of smaller sea urchin-like structure on top of the larger ones.

Figure 4. Reflectance spectra in the UV region of ZnO samples produced from varying concentration of NH₄OH as compared to the reflectance spectra of polished Si.

The density of the nanostructures deposited in the surface of the substrate will lessen the reflectance of the material since large area of SiO₂/Si(100) substrate which is more reflective than ZnO has been covered. Moreover, the reflectances of ZnO obtained are lesser compared to polished silicon. The difference in the reflectance intensity varies in the different region of the spectrum. At 206 nm,
20% reflectance difference is observed while at 220nm the reflectance differs by 28% as compared to the reflectance spectra of ZnO 2M. When compared to the reflectance spectra of ZnO 3M, the reflectance differs by about 25% at 206nm and about 31% at 220 nm. However, at 243 and 289 nm, the reflectance difference is only 6% while at at 265 nm, 282nm and 332 nm, the reflectance is approximately 17%. The significant difference of the reflectance between the obtained sample and polished silicon is an indication that ZnO can be a good material for solar cell applications.

3.2. Effects of thermal annealing

Thermal annealing treatment is the most widely used method to improve the crystal quality of a material. It can affect the crystal structure, grain size and surface quality of thin films because it gives sufficient energy to allow the movement of atoms to occupy the correct site in the crystal lattice [12]. Moreover, annealing is done to eliminate the impurities present in the samples. The annealing time done in our samples is 2 hours and the annealing temperature is 400°C because at around 150°C the suspected impurities present in the samples such as water and Zn(OH)\(_2\) will be decomposed [9]. To examine the effects of thermal annealing treatment, the sample is subjected to SEM-EDS and UV-vis spectroscopy.

Figure 5 shows the high magnification SEM images of ZnO deposited on SiO\(_2\)/Si(100) substrate from 0.03M ZnSO\(_4\) and 2M NH\(_4\)OH annealed at 400°C for 2 hours as compared to an as-deposited sample. After annealing, it can be observed that nanorod formations and sea urchin-like structures are still present as shown in Figures 5 (b). The average diameter of the rods increases up to 783nm which is larger compared to the average diameter of the as-grown sample. After the heat treatment, the diameter of the rods is almost uniform compared to the as-grown sample shown in Figure 5 (a) wherein the diameter of individual rods is not uniform. These observations are thoroughly illustrated in Figure 6. It can be observed in Figure 5 (b) that rods tend to coalesce each other to form bigger rods. It is expected that extending the annealing time to longer period might cause the sea urchin-like structures to disintegrate because complete decomposition of the Zn(OH)\(_2\) seed will take place.

![Figure 5](image)

**Figure 5.** SEM micrographs of ZnO grown on SiO\(_2\)/Si(100) substrate from 0.03M ZnSO\(_4\) and 2M NH\(_4\)OH (a) as-grown and (b) annealed at 400°C for 2 hours.

Figure 6 (a) represents an as-grown ZnO sample before subjected to heat treatment. It is composed of irregularly-sized sea urchin-like structures and nanorods. It is believed that the smaller sea urchin-like structures and nanorods are unstable and will coalesce to other nanorods to form bigger-sized nanorods when applied by high annealing temperature as illustrated in Figure 6 (b). As mentioned above, this high-temperature annealing will provide enough amount of energy to allow the dissociated ZnO atoms to form into a more stable structure. This causes the uniformity and the increase of the
diameter of the nanorods. This phenomenon is known as Ostwald ripening [13, 14]. Moreover, coalescence has taken place where two or more nanorods stick together. Figure 6 (c) is an illustration of the sample after annealing. It is assumed to be composed of thermodynamically stable and pure ZnO rods with nanorod diameter larger by about 53% compared to the as-grown ZnO.

Figure 7 shows the reflectance spectra obtained from as-deposited and annealed ZnO samples shown in Figure 5. It can be observed that similar peaks are present. Furthermore, between 200 to 300 nm, it can be seen that there is a significant difference in their reflectances. The annealed ZnO shows lesser reflectance compared to the as-deposited one. Specifically, 5% reflectance reduction is observed between 200 to 245nm range. It decreases to 3% between 245 to 290nm but minimized to only 1% reduction between 290 to 400 nm. Thermal treatment at 400°C might have caused the decrease in the intensity of reflectance since some of the impurities such as H₂O and Zn(OH)₂ has decomposed. This suggests that the sample is purified after the heat treatment. Moreover, at 206 nm, 20% reflectance difference is observed between polished Si and the as-grown sample while at 220nm the reflectance differs by 25% as compared to the reflectance spectra of the as-grown sample. When compared to the reflectance spectra of the annealed sample, the reflectance differs by about 24% at 206nm and about 28% at 220 nm. However, at 243 and 287 nm, the reflectance difference is only 6% and 10%, respectively, while at 265nm and 333 nm, the reflectance is approximately 17% with respect to the as-grown sample. It is widely known that pure ZnO has lesser reflectance compared to Si as it can be used as window layer for solar cells [15].

![Figure 6](image_url)

**Figure 6.** Formation mechanism of ZnO sample obtained from 2M NH₄OH annealed at 400°C: (a) before annealing, (b) during annealing where smaller, thermodynamically unstable clusters will coalesce spontaneously to allow growth of larger, thermodynamically stable rods, (c) thermodynamically stable and pure ZnO rods.
Meanwhile, Figure 8 shows the high magnification SEM images of ZnO deposited on SiO$_2$/Si(100) substrate from 0.03M ZnSO$_4$ and 3M NH$_4$OH annealed at 400°C for 2 hours as compared with an as-grown sample. It can be observed that after the annealing process, dense sea urchin-like structures are still present as shown in Figure 8 (b). The average diameter of the rods is measured to be approximately 533 nm. This is larger compared to the average diameter of the as-grown sample. However, the presence of flakes covering the sea urchin-like structures is still visible but minimal compared to that of the as-grown sample. Unlike for the annealed ZnO sample obtained from 2M NH$_4$OH concentration, it can also be observed that the sizes of the smaller sea urchin-like structures accumulating on top of the larger ones have become larger instead of coalescence to other nanorods. After annealing, it shows that the diameters of the rods have become larger and the sizes of the urchins have become bigger. This phenomenon is illustrated in Figure 9.

![Figure 7](image7.png)

**Figure 7.** Reflectance spectra in the UV region of as-grown (red) and annealed (blue) ZnO samples obtained from 2M NH$_4$OH concentration.

![Figure 8](image8.png)

**Figure 8.** SEM micrographs of ZnO grown on SiO$_2$/Si(100) substrate from 0.03M ZnSO$_4$ and 3M NH$_4$OH (a) as-grown and (b) annealed at 400°C for 2 hours.
Figure 9 (a) shows an as-grown ZnO. It is characterized by densely-packed sea urchin-like structures. On top of the larger sea urchin-like structures are smaller sea urchin-like structures that are covered with appreciable amount of flakes which are believed to be impurities. Upon annealing, Ostwald ripening will take place which might cause the diameter of the rods to increase and the amount of flakes to be minimized as shown in Figure 9 (b). The flakes might have contributed to the enlargement of the diameter of the nanorods. At high temperature (400°C), unstable molecules will dissociate. The dissociated atoms will eventually associate to other existing ZnO nanorods to form a more stable structure. Furthermore, the smaller sea urchin-like structures have become larger. Figure 9 (c) illustrates the sample after subjected to annealing treatment. It is assumed to be comprised of thermodynamically stable and partially purified ZnO rods with 13.40% increase in nanorod diameter and bigger sea urchin-like structures as compared to the as-deposited sample. The dominant elements present are Zn, O and Si. The Zn to O ratio for the annealed sample is close to the stoichiometric ratio of ZnO.

![Figure 9](image)

**Figure 9.** Formation mechanism of ZnO sample obtained from 3M NH₄OH annealed at 400°C: (a) before annealing, (b) during annealing where flakes and other thermodynamically unstable clusters will dissolve spontaneously to allow growth of larger, thermodynamically stable rods, (c) thermodynamically stable and partially purified ZnO rods.
Shown in Figure 10 are the reflectance spectra of the annealed and unannealed ZnO sample obtained from 3M NH₄OH concentration in comparison with that of polished silicon. It can be noticed that the unannealed and annealed samples have similar peaks and the intensity of their reflectance differs to only about 2% with the annealed sample having lower reflectance. This implies that the sample is not completely purified. This can be explained by the incomplete decomposition of the impurities (i.e., flakes). In addition to that, the ZnO samples have lower reflectance compared to polished silicon. This observation is similar to what is observed in the previous samples. At 206 nm, 26% reflectance difference is observed while at 220 nm the reflectance differs by 32% as compared to the reflectance spectra of the as-grown sample. When compared to the reflectance spectra of the annealed sample, the reflectance differs by about 27% at 206 nm and about 32% at 220 nm. However, at 243 and 289 nm, the reflectance difference is only 10% while at 265 nm, 282 nm and 332 nm, the reflectance is approximately 18% both for the annealed and as-grown samples.

![Figure 10. Reflectance spectra in the UV region of as-grown (red) and annealed (green) ZnO samples obtained from 3M NH₄OH concentration.](image)

4. Summary and conclusion

ZnO nanostructures were successfully produced on SiO₂/Si(100) using chemical bath deposition method. The effects of concentration of NH₄OH and thermal annealing were investigated. It was observed that ZnO grown from varying concentration of NH₄OH shows variation in the density of the nanostructures. The density increases as the concentration of NH₄OH is increased. However, the diameter of the rods decreases as the concentration of NH₄OH is increased. The intensity of the reflectance in the UV region decreases as the concentration of NH₄OH is increased. It can be further observed that there is a competition of the ion-by-ion growth mechanism and hydroxide cluster mechanism in bath with 2M NH₄OH concentration while bath with 3M NH₄OH concentration is dominated by the hydroxide cluster growth. SEM images of the thermally annealed ZnO samples reveal that the diameter of the rods increases after annealing the sample at 400°C due to Ostwald ripening. The reflectance shows that annealing reduces the reflectance of the sample since at this time pure ZnO is obtained. Only oxygen, zinc, and silicon were detected. The silicon element comes from the substrate. This confirms that the nanorods are primarily ZnO. Moreover, the growth mechanisms of ZnO formation for different experimental conditions have been illustrated.
5. References

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