Two-stage Process on the Growth of High-density Zinc Oxide Nanostructures via Chemical Bath Deposition on Glass Substrates

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Abstract

Zinc oxide nanostructures were deposited on glass substrates using $ZnSO_4$ with varying NH_4OH concentration via one-stage and two-stage chemical bath deposition (CBD) method. The two-stage process was prepared by pre-treatment of the glass substrates with ZnO colloid powder which were obtained from a previous bath deposition before the CBD takes place. Scanning electron microscope (SEM) images revealed that the two-stage CBD technique yielded a high-density of the ZnO nanostructures as compared to the one-stage process. Moreover, the growth of ZnO nanostructures exhibits a hexagonal structure as revealed by the SEM images. The growth of high-density ZnO nanostructures via two-stage CBD technique can be explained by the presence of the early nucleation of ZnO nuclei provided during the pre-treatment of the substrate with ZnO colloid powders. Furthermore, annealing the as-grown nanostructures at 200^oC resulted into the decomposition of Zn complexes forming high-quality ZnO nanostructures and coalescence of smaller ZnO nanostructures to formed bigger ones also occurred. Higher absorption spectra can also be observed from the nanostructures grown via the two-stage process which further confirms the growth of high-density ZnO nanostructures. The calculated energy band gap extracted from the UV-Vis spectra is in good agreement with the reported energy band gap of ZnO nanostructures.

***Keywords**:* ZnO, two-stage process, CBD, SEM, annealing

1. Introduction

Over the past years, there have been intensive works in the growth of zinc oxide (ZnO) nanostructures. ZnO is one of the semiconductor materials which has received much attention in the research community because of its large direct band gap of 3.37 eV at room temperature, large exciton binding

energy of 60 meV, and excellent chemical and thermal stability (Yang *et al.*, 2009). It has been recognized as one of the promising nanomaterial in a wide range of potential applications such as short wavelength electro-optical devices, gas sensors, dye-sensitized solar cells, transistors and field emission displays (Tay *et al.*, 2009; Kim *et al.*, 2010; Kumar *et al.*, 2018; Khranovskyy and Yakimova, 2012). Moreover, because of its biocompatibility, it has also been used in drug delivery, cancer treatment, bio-imaging, and antibacterial products (Arya *et al.*, 2012).

However, different specific device application requires different size distributions and density of the ZnO nanostructures. For instance, the proliferation suppression ability of ZnO nanoparticles on cancer cells are size-dependent, which will need the smaller nanoparticle size for the higher cytotoxicity of cancer cell proliferation caused by the ZnO nanoparticles (Li *et al.*, 2010). The antibacterial activity of ZnO nanostructures is influenced by factors such as the particle size and the specific surface area of the nanostructures (Subhasree *et al.*, 2012). On the other hand, gas sensors use the effective surface area for gas adsorption, and this requires dense growth of nanostructures. Electronic devices based on the piezoelectric property of the ZnO nanorods will require gaps between the rods to get sufficient deformation for generating the required voltage (Baruah and Dutta, 2009). Higher conversion efficiency for solar cells can be ascribed to good alignment and higher coverage density of the nanostructures (Liu *et al.*, 2010). Extensive studies on controlling the morphology and surface architecture of the ZnO nanostructures is significant to tailor for specific device application.

Controlling the size distribution and density of ZnO nanostructures is one of the most challenging tasks for achieving the desired physical properties for specific device applications. It was revealed that ZnO nanostructures could be grown with varying diameters and lengths using a hydrothermal method by just controlling the pH of the reaction bath (Baruah and Dutta, 2008; Suresh and Kumar, 2012). It is believed that the pH of the bath plays a significant role in the growth morphology and dimensions of the nanostructures. On the other hand, ZnO nanorods can be grown with controlled dimension, areal density, and surface morphology by incorporating a simple ionic additive that will act as a growth modifier (Downing *et al.*, 2013). Moreover, the size of the ZnO nanostructures can be controlled by incorporating a catalyst during the chemical bath deposition (Shinagawa *et al.*, 2011). This catalyst will act as a seed layer for the growth of ZnO nanorods. It has been reported that growth of ZnO nanostructures

will be influenced by the introduction of ultrasonic treatment (Zhang *et al*., 2013). It is believed that using fore-ultrasonic treatment is beneficial to form the nucleus of the nanorods with varying length and diameter and the post-ultrasonic treatment can change the state of the morphology of the ZnO nanorods.

Another way to control the growth of ZnO nanostructures is with the use of substrate seeding before the deposition process that will eventually control the size and shape of ZnO nanorods (Liu *et al.*, 2010; Rodriguez *et al.*, 2013). There were reports that pre-synthesized seeds have been used to produce smaller and denser ZnO nanostructures. This seed layer will provide nucleation centers for the growth of ZnO nanostructures. However, previous reports utilized solution-based sol-gel seed by spin-coating. This needs an additional chemical process to prepare the sol-gel, thus making the method more complicated. Furthermore, mostly reported seed layers use other chemicals other than precursor chemicals used for the chemical bath deposition thus making the process more costly.

In this paper, the growth of ZnO nanostructures was done by providing a seed layer on the glass substrate that will utilize the filtered ZnO colloid powders obtained from a previous chemical bath deposition. This is a simple process that will provide a nucleation center that eventually controls the size and density of ZnO nanostructures.

2. Methodology

ZnO nanostructures were deposited on a glass substrate using chemical bath deposition (CBD) via one-stage and two-stage process. The two-stage process was prepared by providing a seed layer before the CBD takes place. The seed layer used was ZnO colloid powders obtained from a previous CBD. These colloid powders were coated evenly on one side of the glass substrate using a spatula. The reagents that were used were aqueous zinc sulfate ($ZnSO_4$) and aqueous ammonium hydroxide (NH_4OH) concentration. The concentration used for $ZnSO_4$ was kept constant at 0.03 M while the NH_4OH concentrations were varied to 1.0 M and 3.0 M. The samples were characterized using scanning electron microscope (SEM) and ultraviolet-visible spectroscopy (LAMBDATM 35 UV-Vis).

3. Results and Discussion

3.1 Fomation of ZnO Nanostructures via Two-stage Process

The morphology of ZnO nanostructures deposited on the glass substrates prepared from 1.0 M NH_4OH concentration and grown via one-stage process and a two-stage process is shown in Figure 1. Formation of hexagonal nanostructures is present in both samples. Figure 1 (a) shows the SEM micrographs of ZnO nanostructures grown via a one-stage process. It is observed that few nanostructures are deposited on the substrate. These observed nanostructures show clusters of nanorods which exhibit sea-urchin like formations. Their lengths vary in sizes with average radius found to be around 160 – 180 nm. On the other hand, Figure 1 (b) depicts the ZnO nanostructures grown via a two-stage process. It is observed that growth of ZnO nanostructures has a higher density as compared to the ZnO nanostructures grown via a one-stage process. These nanostructures have different length and grow in random directions. It was found the average radius of the grown nanostructures ranges from 170 – 200 nm.

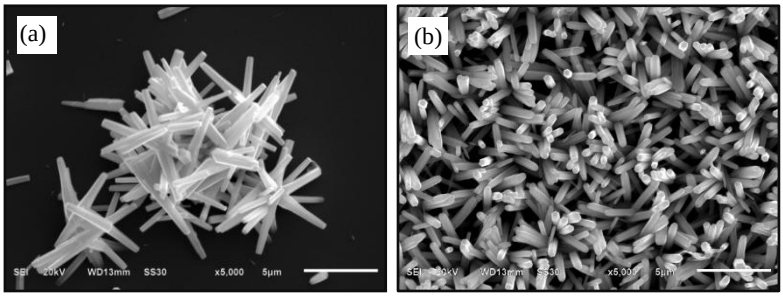


Figure 1. SEM micrographs of ZnO nanostructures which were grown on glass substrates which are grown via one-stage process (a) and two-stage process (b) prepared from 1.0 M NH_4OH concentrations at lower magnification and higher magnification.

For effect of using different NH_4OH concentration on the surface morphology of the nanostructures to be observed, the NH_4OH concentration was increased to 3.0 M. Figure 2 shows the SEM images of the ZnO nanostructures deposited on glass substrates via one-stage and two-stage process prepared with 3.0 M NH_4OH concentration. Figure 2 (a) depicts the formation of the ZnO nanostructures via a one-stage process. It is observed that formation of sea-urchin like nanostructures is present. However, some

portion of the substrates does not have ZnO nanostructure formation. The average radius of these nanostructures was found to be around 140–190 nm. On the other hand, ZnO nanostructures grown via two-stage process are shown in Figure 2 (b) where the formation of denser ZnO nanostructures can be observed with network formations. It is also observed that the grown ZnO nanostructures have a hexagonal shape with an average radius of about 230 – 250 nm. The network formations might be attributed to the presence of zinc hydroxide complexes.

The higher density of growth of the nanostructures grown via two-stage process both in 1.0 M and 3.0 M NH_4OH concentrations is believed to be brought by the early nucleation provided by the pre-treatment of the glass substrate with ZnO colloids. These early nucleation sites attracted more ZnO molecules in the bath because it is easier for the incoming ZnO molecules to join the pre-grown ZnO through Van der Waals force of attraction. The treatment of seed layers on the substrate in the two-stage process provides nucleation sites which might lower the thermodynamic barrier to formation hence resulting in lowering total free energy in the formation of the ZnO nanostructures. As a result, the formation of a higher density distribution of ZnO nanostructures is observed.

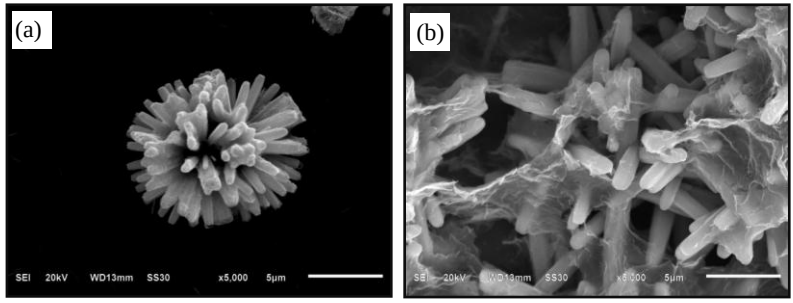


Figure 2. SEM micrographs of ZnO nanostructures on glass substrates which were grown via one-stage process (a) and two-stage process (b) prepared from 3.0 M NH_4OH concentrations at lower magnification and higher magnification.

3.2 Effects of Annealing on the Grown ZnO Nanostructures

For the effect of annealing on the grown ZnO nanostructures to be observed, the as-grown ZnO samples were annealed at 200^{o}C for one hour. This annealing process is said to decompose the presence of Zn complexes in the nanostructures which will produce higher quality nanostructures (Mutia and

Alguno, 2013). Figure 3 shows the SEM images of the annealed ZnO nanostructures grown on glass substrates via one-stage process and via two-stage process prepared from 1.0 M NH_4OH concentration. It is expected that decomposition and coalescence of smaller nanostructures to form bigger nanostructures will be formed.

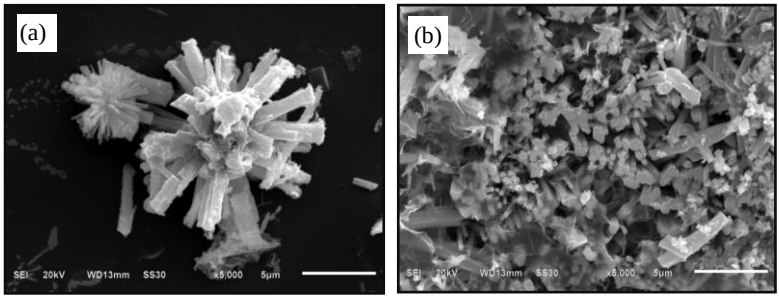


Figure 3. SEM images of ZnO nanostructures on the glass substrate which were grown via (a) one-stage process and (b) two-stage process prepared with 1.0 M NH_4OH concentration at lower and higher magnifications after thermal annealing.

The average radius of the nanostructures grown via one-stage process is found to be around 220 – 250 nm. An increase in average size was observed after thermal annealing at 200^{o}C. On the other hand, the average radius of the ZnO nanostructures grown via two-stage process is about 200 – 270 nm. The coalescence of smaller nanostructures to form bigger nanostructures is also observed. This phenomenon has been reported as Ostwald ripening (Madras and McCoy, 2002). This Ostwald ripening is a coalescence of a smaller particle to a bigger particle to exist at a higher temperature. The effect of thermal annealing at 200^{o}C with the nanostructures prepared from 3.0 M NH_4OH is shown in Figure 4. As observed in the SEM images shown in Figure 2 before thermal annealing, the presence of flake-like networks is observed. This flake-like networks vanished after the introduction of thermal annealing. This might suggest that the flake-like networks are composed of Zn complexes that may have decomposed during thermal annealing. Dissociation of Zn complexes to form high-quality ZnO nanostructures is expected. The average radius after thermal annealing increased as expected.

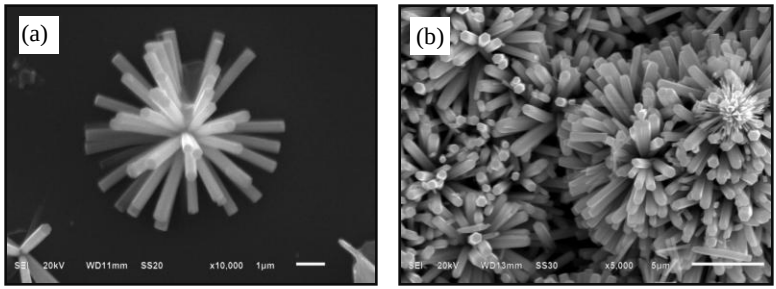


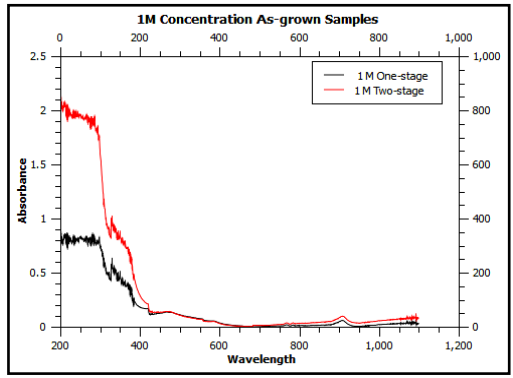
Figure 4. SEM images of ZnO nanostructures on the glass substrate which were grown via (a) one-stage process and (b) two-stage process prepared with 3.0 M NH_4OH concentration at lower and higher magnifications after thermal annealing.

3.3 Absorbance Spectra of the Grown Nanostructures

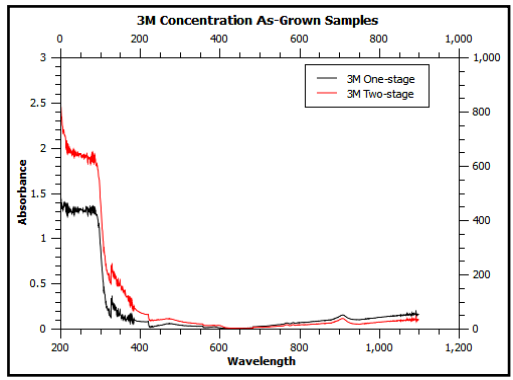
Optical absorbance spectra of the synthesized ZnO nanostructures deposited on glass substrates were plotted as a function wavelength in the range 200 nm – 1100 nm using ultraviolet-visible spectroscopy.

Figure 5 represents the graph of the absorbance spectra of the different samples of the grown ZnO nanostructures. The absorbance spectra of the nanostructures grown via one-stage and two-stage CBD process were superimposed to see the difference in their absorbance spectra. As observed, there are higher absorption spectra in the wavelength of range 300 nm to 400 nm, which is in the ultraviolet region, for the nanostructures grown via two-stage CBD process. The range 300 nm to 400 nm is believed to be the range which shows that ZnO nanostructures are successfully grown. Higher absorption spectra in the nanostructures grown via two-stage process coincide with the results of the images obtained from SEM images which shows us that there is a higher density distribution in the ZnO nanostructures synthesized via the two-stage CBD process.

The absorption process happens when a quantum energy of light passing through a material is used to promote electrons from the ground state to one of its excited states. Since excited states are unstable, the excited electrons will rapidly revert to the ground state losing the acquired energy in the process. This is the absorption spectra of the material that is referred to in the graphs. Since there is more contact surface area for the incoming incident light in the nanostructures grown via two-stage process, more electrons are also promoted to the excited states resulting to higher absorption of the nanostructures.



(a)



(b)

Figure 5. Superimposed absorbance of spectra of ZnO nanostructures which were grown via one-stage and two-stage CBD process (a) as-grown samples prepared from 1.0 M NH_4OH concentration (b) as-grown samples prepared from 3.0 M NH_4OH concentration.

The high absorption of the ultraviolet region by the nanostructures suggest that the energy associated with the wavelength in the range of the ultraviolet region is just right to promote the electrons from the ground state to one of its excited states.

Optical reflectance spectra of the synthesized ZnO nanostructures deposited on glass substrates were also potted as a function of photon energy in the range 200 nm – 1100 nm using ultraviolet-visible spectroscopy. Using Tauc's equation versus photon energy, the energy band gap of the grown ZnO nanostructures were extrapolated. Through linear fitting, the extrapolated value is around ~3.24 eV for both the 1.0 M and 3.0 M

concentration as-grown and annealed samples. This is in good agreement of the reported band gap of ZnO.

4. Conclusions

One-stage and two-stage process chemical bath deposition techniques were used to grow the ZnO nanostructures on glass substrates using $ZnSO_4$ with varying concentration of NH_4OH. The as-grown ZnO nanostructures and annealed ZnO nanostructures at 200^oC were characterized using SEM-EDX for surface morphology and elemental composition analysis, UV-Vis spectroscopy for absorbance measurements and extracting the energy band gap of the grown ZnO nanostructures.

Clusters of ZnO nanostructures with urchin-like morphology was observed in the nanostructures grown on glass substrates via one-stage process prepared from both 1.0 M and 3.0 M NH_4OH concentrations. On the other hand, the nanostructures grown on glass substrates via two-stage process showed a significant increase in the density distribution of the nanostructures. The increase in the density distribution of the grown nanostructures can be explained by the early nucleation provided by the pre-treatment of the glass substrates with ZnO colloid powders obtained from a previous CBD. This early ZnO nuclei attracted more incoming ZnO molecules from the bath because of Van der Waals forces of attraction. Also, these nucleation sites might lower the thermodynamic barrier to formation hence resulting in lowering total free energy in the formation of the ZnO nanostructures.

The effect of thermal annealing on the as-grown nanostructures at 200^oC for one hour as revealed by the SEM images of the nanostructures prepared at 1.0 M NH_4OH showed decomposition of Zn complexes in the nanorods and coalescence of smaller nanostructures to form bigger ones. It is also revealed that slight increase in the radius of the ZnO nanostructures was observed. On the other hand, the effect of annealing the nanostructures prepared from 3.0 M NH_4OH concentration decomposed the flake-like network formations believed to be Zn complexes. The absorption spectra of the nanostructures grown on glass substrates via two-stage process revealed higher spectra which strongly supports the agreement that there is a growth of higher

density ZnO nanostructures as compared to the nanostructures grown via the one-stage process.

5. References

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