MATEC Web of Conferences **27**, 02007 (2015)
DOI: 10.1051/matecconf/20152702007

Effect of Solution pH and $ZnCl_2$ on Zinc Oxide Nanostructures Grown on Zn Foil

Christian Mark Pelicano[a], Mary Donnabelle Balela[b]

Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines

Abstract. Zinc oxide (ZnO) nanostructures were formed by wet oxidation of zinc (Zn) foil in water at 90°C for 4 h. The effect of pH and $ZnCl_2$ concentration on the morphology and structure of the resulting ZnO nanostructures on the surface of Zn foil were investigated. Clusters of ZnO nanosheets were visibly grown on top of hexagonal flat-topped nanorods in the presence of 0.05 M $ZnCl_2$. Addition of higher $ZnCl_2$ concentration resulted to layered plate-like structures of simonkolleite compound ($Zn_5(OH)_8Cl_2 \cdot H_2O$). The formation of this compound is favored at high concentrations of Zn^{2+} and Cl^- ions. In addition, flower-like structures of hexagonal nanorods, coarse nanorods and nanotubes were obtained at increasing pH values from 6.3 to 10. The increased concentration of OH^- ions possibly hindered further deposition of hydrolyzed Zn(II) ions and the subsequent dissolution and redeposition of the existing ZnO nanostructures directed the formation of coarse nanorods and nanotubes.

1 Introduction

Nanostructured zinc oxide (ZnO) has been extensively studied as potential material in broad range of applications, namely gas sensors, photocatalysis, solar cells, and light emitting diodes among others. ZnO is a well-known n-type semiconductor having a wide band gap of about 3.37 eV and a large exciton binding energy of about 60 meV at room temperature [1]. It has been well established that the properties of nanostructured ZnO depend strongly on its structural morphology, crystal size and crystalline density [2]. To date, different ZnO nanostructures, such as nanowires [3], nanotubes [4], nanorods [5], and nanodisks [6] have been synthesized by various methods including vapor phase deposition [7], thermal oxidation [8], electrochemical methods [9], and hydrothermal process[10]. However, reaction conditions, such as high temperature, accurate gas concentration, toxic chemical reagents, and costly equipment, limit the extent of application of ZnO nanostructures using the above techniques. The challenge now is to develop a facile and cost-effective approach which can be easily up-scaled for commercial application.

Herein, ZnO nanostructures are prepared at a low temperature wet oxidation of Zn foil in aqueous solution. This technique could pave way to the fabrication of flexible optoelectronic devices on substrates with low thermal stability. Contamination can also be prevented since only water is needed to initiate ZnO nanostructure formation. Previous studies by Chen et al. revealed the effect of water vapor on ZnO formation [11-12]. Tan et al. also reported the influence of growth time on the morphology ZnO nanostructures using hot water oxidation of etched Zn foils [13]. In our previous study, the effects of etching and oxidation time on the ZnO nanostructures were examined [14].Hemispherical ZnO structures composed of nanorods and nanotubes were obtained on the surface of etched Zn foil with increasing reaction time, whereas only aligned nanorods were produced on pristine Zn foil. In this work, the effects of solution pH and Zn(II) addition on the morphology and structure of the resulting ZnO nanostructures were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively.

2 Experimental

Zn (99.95%, Nilaco, 1.5x1.5x0.05 cm) foils were used as the starting material. First, they were ground using silicon carbide paper with increasing grit sizes and then polished with alumina powder to remove native oxides. The samples were then cleaned with acetone in an ultrasonic bath for 10 min to remove impurities from the polishing process. Before wet oxidation, the foils were etched in 5% hydrochloric acid (HCl, Sigmal Aldrich) in ethanol (Sigma Aldrich) solution for 3 min. Subsequently, the etched Zn foils were immersed in 400 ml of deionized water at 90 °C for 4h. To investigate the influence of zinc chloride ($ZnCl_2$, Sigma Aldrich) increasing concentrations of $ZnCl_2$ (0.05 to 0.40M) were added into the hot water during wet oxidation~~.~~ On the other hand, the solution pH was adjusted from 4 to 10 at room temperature by adding amounts of nitric acid (HNO_3, Sigma Aldrich) or ammonia (NH_3, Sigma Aldrich). The morphology of the ZnO nanostructures was observed in a scanning electron microscope (SEM, JEOL JSM 5300).

Corresponding author: [a] copelicano@upd.edu.ph, [b] mdlbalela@gmail.com.

The crystal structure of the ZnO samples was determined by X-ray diffraction (XRD, Siemens Kristalloflex 760) using Cu Kα.

3 Results and discussion

Figure 1 shows the SEM images of the surface of Zn foil after wet oxidation at 90 °C for 4 h with increasing $ZnCl_2$ concentrations. Flat-topped hexagonal nanorods and nanosheets forming flower-like structures were obtained at 0.01M $ZnCl_2$ as seen in Fig. 1(a). The nanorods have a mean diameter of 300 nm, while the nanosheets have a non-uniform thickness of about 30 nm. Interestingly, the ZnO nanosheeets were observed to be lying on top of the hexagonal nanorods. It has been shown that clusters of hexagonal nanorods were produced after oxidation of etched Zn foil in hot water at 90 °C for 4h as in the inset of Fig. 1(a) [14].

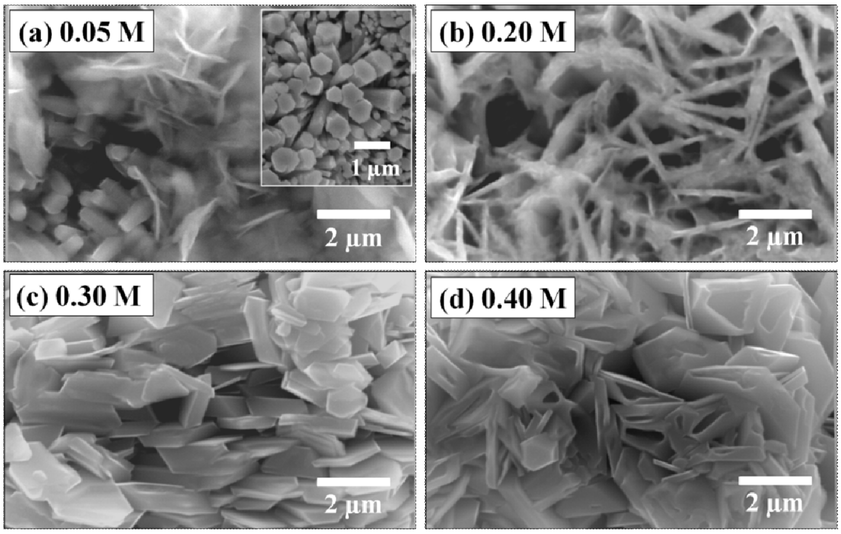

Figure 1. SEM images of the Zn surface obtained after wet oxidation at different $ZnCl_2$ concentrations: (a) 0.05M, (b) 0.20M, (c) 0.30M and (d) 0.40M.

During oxidation of Zn foil in water, Zn^{2+} aquo ions are released in the solution, particularly from the ridges and grain boundaries produced by etching. These imperfections act as diffusion paths for the Zn^{2+} ions from the Zn substrate. On the other hand, the partial cathodic reactions, i.e. reduction of dissolved oxygen (O_2) and hydrogen (H_2) gas evolution, supply hydroxyl ions (OH) that leads to the increase in the local pH near the vicinity of the Zn foil. This promotes the growth of ZnO layer through the hydrolysis of Zn(II), specifically on the ridges and grain boundaries on the surface of the Zn metal. Zn(II) refers to all Zn(II) species in the solution, such as Zn^{2+} aquo ions, Zn(OH) , $HZnO_2$, etc. On the other hand, the hexagonal-shaped of the nanorods can be attributed to the crystal structure of the resulting ZnO after wet oxidation. The thermodynamically stable phase of ZnO at low temperature is the wurtzite structure. It has been well established that wurtzite ZnO has polar ± (0001) and non-polar {2110} {0110} planes. Polar Zn-terminated (0001) planes are metastable and chemically active, while the non-polar planes have lower energies and inert [15]. Hence, anions such as OH ions would be adsorbed specifically onto the polar Zn-terminated (0001) positive plane creating one-dimensional ZnO nanostructures like the nanorods in Fig. 1(a). Since $ZnCl_2$ is added in the solution, there is an increase in the total activity of Zn(II) ions. These extra Zn(II) could easily react with OH , which could generate large clusters of ZnO nanoparticles in the solution [16]. However, the presence of Cl possibly shields the polar (0001) planes from the OH ions. Deposition of Zn(II) occurs in all directions, leading to the formation of ZnO nanosheets. Additionally, the existing nanorods on the surface possibly act as seeds for the growth of the nanosheets. This results to the deposition of the nanosheets on top of the hexagonal nanorods. When the concentration of $ZnCl_2$ is increased to 0.20 M, nanoflakes with thickness ranging from 170-280 nm are formed.The nanoflakes appear coarse, suggesting that the hydrolyzed Zn(II) ions deposits on the surface of the initial nanosheets.The hexagonal nanorods are no longer observed. It is possible that the large clusters of nanosheets fully cover the underlying ZnO nanorods. Moreover, hexagonal plate-like structures were produced at 0.30M $ZnCl_2$. The nanoplates have a mean thickness of about 390 nm and an average diameter of about 2.5 μm. Further increasing the $ZnCl_2$ amount to 0.40 M results in the possible coalescence of the nanoplatelets into a layered structure as in Fig. 1(d).

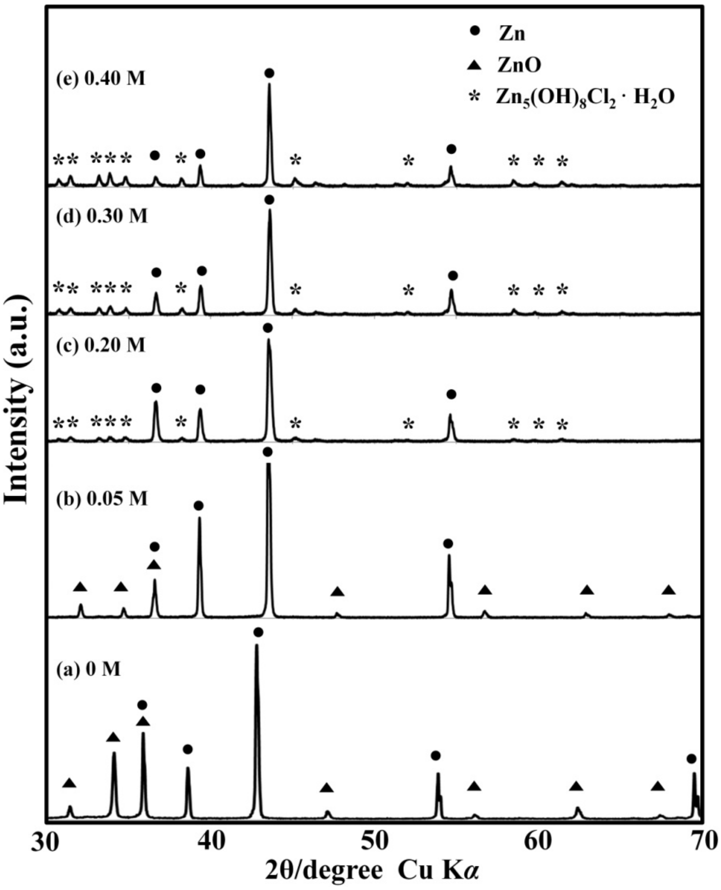

Figure 2. XRD patterns of the Zn foils after wet oxidation at different $ZnCl_2$ concentrations: (a) 0 M, (b) 0.05M, (c) 0.20M, (d) 0.30M and (e) 0.40M.

Fig. 2 shows the XRD patterns of the samples prepared at different $ZnCl_2$ concentrations. As seen in Fig. 2(a)-(b), the peaks at 31.96 °, 34.60 ° and 36.52 ° can be indexed to the 100, 002, and 101 peaks ZnO wurtzite structure (JCPDS 36-1451, a= 3.2249 Å, c= 5.206 Å), respectively. No other peaks except from the underlying metallic Zn substrate are observed. This agrees well with the morphology of synthesized ZnO nanostructures in Fig. 1(a). However, the diffraction peaks in Fig. 2(b) slightly shifted to higher 2θ values indicating a decrease in the interplanar spacing of the ZnO crystals. The calculated lattice constants are a= 3.2229 Å and c= 5.1786 Å. This is possibly due to the interfacial compressive strain induced by the formation of ZnO nanosheets on top of the nanorods. Compared to the XRD pattern of the hexagonal nanorods in Fig. 2(a), the intensities of the 100 and 101 peaks appear stronger than the 002 peak in the diffraction pattern for the mixed nanorods and nanosheets in Fig. 2b. This supports the possible growth of the ZnO nanosheets due to the large concentration of Cl adsorbed onto the polar (0001) plane. For higher concentrations of $ZnCl_2$ from 0.20 – 0.40 M, all the diffraction peaks except those for the Zn substrate can be attributed to the hexagonal phase of $Zn_5(OH)_8Cl_2 \cdot H_2O$ or simonkolleite compound (JCPDS 07–0155). Simonkolleite is typically produced when the concentration of the Zn^{2+} ions exceeds 0.01 M and its structures are usually layered hexagonal platelets which is similar to the morphology of the products in Fig. 1(b)-(d) [17].

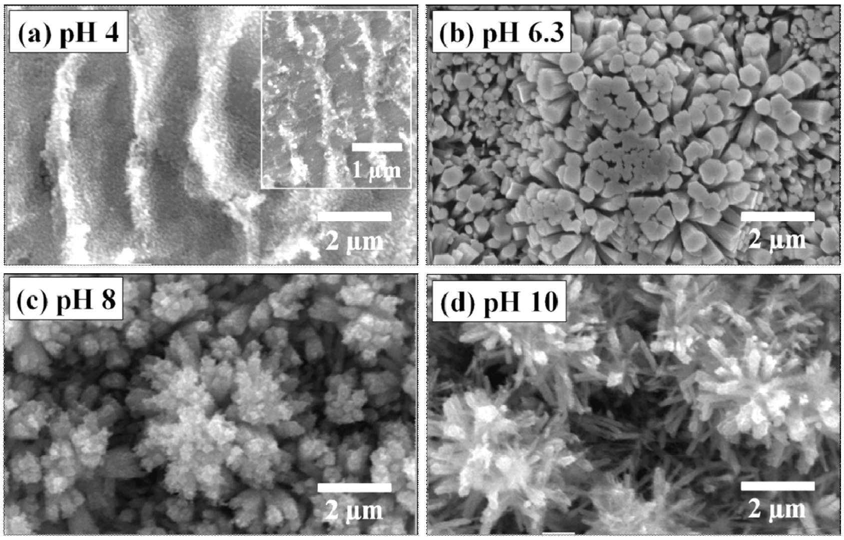

Figure 3. SEM images of the etched Zn surface after oxidation in water for 4 h at 90 °C under different pH: (a) pH 4, (b) pH 6.3, (c) pH 8, and (d) pH 10.

The surface morphologies of etched Zn foil after wet oxidation in water for 4 h at 90 °C under different pH conditions are shown in Figure 3. Large grooves and ridges, similar to those formed after etching (see inset of Fig. 3a), are observed after wet oxidation at pH 4. No ZnO nanostructures are formed. It is possible that the acidic condition leads to dissolution of any deposited ZnO product. Additionally, the thermodynamically stable species of Zn at low pH is the Zn^{2+} aquo ions. This could explain the absence of any significant ZnO deposits on the surface. At pH 6.3, hemispherical clusters of hexagonal flat-topped nanorods were formed. The diameter of the nanorods increases outwards with an outermost mean diameter of 440 nm, suggesting outward diffusion of Zn^{2+}. When pH is increased to 8-10, flower-like structures of coarse nanorods and nanotubes are obtained. The formation of ZnO is thermodynamically favored at high pH. However, the diffusion of Zn^{2+} aquo ions from the Zn foil to the surface is hindered as the oxide layer thickens. Additionally, the increased in the OH$^-$ ions due to high pH possibly prevent further deposition of hydrolyzed Zn(II) ions onto the (0001) planes. Consequently, the existing ZnO nanostructures possibly redissolve and redeposit onto the primary ZnO nanorods, leading to the coarse nanorods and nanotubes in Fig. 3(c)-(d).

4 Summary

The effects of solution pH and ZnCl$_2$ on the morphology and structure of ZnO grown by wet oxidation at 90 °C in water for 4h were examined. At 0.05M ZnCl$_2$, flat-topped hexagonal ZnO nanorods and nanosheets were obtained. The nanosheets are formed on top of the nanorods. This suggests that the nanorods are grown from the oxidation of the Zn substrate, whereas the nanosheets are oxidation of extra Zn(II) ions supplied by ZnCl$_2$. Higher ZnCl$_2$ concentrations only formed simonkolleite layered-platelet structures. Changing the solution pH from 6.3 to 10 produced hemispherical structures of nanorods and nanotubes. At acidic condition, etching of ZnO deposits possibly occurs. Thus, no ZnO nanostructures are deposited on the Zn substrate. These results demonstrated that both solution pH and addition of Zn(II) ions could significantly influence the morphology and composition of the product formed during wet oxidation of Zn foil in hot water.

Acknowledgement

The authors would like to thank the Department of Science and Technology Philippine Council for Industry, Energy and Emerging Technology Research and Development (DOST-PCIEERD) and the Engineering Research and Development for Technology (ERDT) for the research assistance.

References

1. Y. I. Ozgur, Alivov, C. Liu et al., “A comprehensive review of ZnO materials and devices,” J. Appl. Phys, **98** (2005), 1–103.
2. J. Z.Yin, et al., Water Amount Dependence on Morphologies and Properties of ZnO nanostructures in Double-solvent System. Sci. Rep. 4, 3736.
3. S. Chu, G. Wang, W. Zhou et al., “Electrically pumped waveguide lasing from ZnO nanowires,” Nat. Nanotechnol, **6** (2011), 506–510.
4. H. Lu et al., “One-step electrodeposition of single-crystal ZnO nanotube arrays and their optical properties”, J. Alloy Compd, **588**, (2014), 217–221.
5. T.-H. Lee et al., “Fast vertical growth of ZnO nanorods using a modified chemical bath deposition”, J. Alloy Compd., **597** (2014), 85–90

6. S. H. Seo and H. C. Kang, “Self-assembled ZnO hexagonal nano-disks grown by radio-frequency magnetron sputtering”, Mater Lett, **94** (2013), 34–37.
7. T. J. Sun and J. Sh. Qiu, “Fabrication of ZnO microtube arrays via vapor phase growth”, Mater Lett, **62** (2008), 1528–1531.
8. W. K. Tan et al., “Oxidation of etched Zn foil for the formation of ZnO nanostructure”, J. Alloy Compd, **509** (2011), 6806–6811
9. D. Ling et al.,“Electrochemical route to the synthesis of ZnO microstructures: its nestlike structure and holding of Ag particles”, Nanoscale Res Lett, **8** (2013), 78.
10. J.-Y. Kim et al., “Hydrothermal fabrication of well-ordered ZnO nanowire arrays on Zn foil: room temperature ultraviolet nanolasers,” J Nanopart Res, **13** (2011), 6699–6706.
11. R. Chen et al., “Growth mechanism of ZnO nanostructures in wet-oxidation process,” Thin Solid Films, **519** (2011), 1837–1844.
12. R. Chen et al., “Zinc oxide nanostructures and porous films produced by oxidation of zinc precursors in wet-oxygen atmosphere,” Materials International, **21** (2011), 81-96.
13. W. K. Tan et al., “Formation of highly crystallized ZnO nanostructures by hot-water treatment of etched Zn foils,” Mater Lett, **91**(2013), 111–114.
14. C. M. O. Pelicano., Z. Lockman, M. D. Balela, “Zinc Oxide Nanostructures Formed by Wet Oxidation of Zn Foil,” Advanced Materials Research, **1043** (2014), pp. 22-26.
15. L. Vayssieres et. al., “Three-Dimensional Array of Highly Oriented Crystalline ZnO Microtubes,” *Chem. Mater.*, **13** (2001), 4395–4398.
16. W. K. Tan et al., “Synthesis of ZnO nanorod–nanosheet composite via facile hydrothermal method and their photocatalytic activities under visible-light irradiation,” J. Solid State Chem., **211** (2014), 146–153.
17. D. Pradhan and K. T. Leung, “Controlled growth of two-dimensional and one-dimensional ZnO nanostructures on indium tin oxide coated glass by direct electrodeposition,” Langmuir. **24**, (2008), pp. 9707-9716.