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Full Length Research Paper

Cluster-assembled ZnO films prepared by electrochemical deposition on copper substrate

Sucheewan Krobthong[1], Auttasit Tubtimtae[1], Chawalit Bhoomanee[2], Supab Choopun[2], Suphadate Sujinapram[1] and Sutthipoj Sutthana[1]*

[1]Department of Physics, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen Campus, Nakhon Pathom 73140, Thailand.
[2]Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiangmai 50200, Thailand.

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Cluster-assembled ZnO films were synthesized by using electrochemical deposition technique with various reaction times. Zinc nitrate dissolved in de-ionized water was used as a precursor of ZnO film. The as-synthesized cluster-assembled ZnO films were performed on a copper plate used as a substrate at room temperature. The stabilized high electric field of 4 kV/m was applied in the process. Field emission scanning electron microscopy (FE-SEM) was used to characterize the film morphology. The FE-SEM micrographs showed that the surface morphologies of ZnO films are clustered-like structures with aggregated nascent particles when the reaction time was increased. An energy dispersive x-ray spectroscopy (EDS) was used to monitor the films composition, consists of Zn and O with contamination-free composition and an x-ray diffractometry (XRD) showed the x-ray signal patterns of ZnO film incorporating hexagonal wurtzite crystal structures.

Key words: Cluster-assembled ZnO films, copper substrate, electrochemical deposition.

INTRODUCTION

Zinc oxide (ZnO) is one of the most important functional materials that researchers have been attracting much attention to use in a variety of electronic devices due to their novel properties of excellent chemical and thermal stability and potential application such as gas sensors (Shouli et al., 2011), solar cell (Luo et al., 2011), optoelectronics (Djurišić et al., 2010), transistors (Wolff and Hilleringmann, 2012), light emitting diodes (Gupta et al., 2011), photodetectors (Chen et al., 2009), photocatalyst (Akyol and Bayramoglu, 2010). ZnO has a wide direct band gap semiconductor at room temperature with high quality of crystallinity in c-axis oriented structures and electron mobility are favorable to increase of electron transport optimization. Various efforts of physical deposition techniques have been previously reported in the preparation of ZnO to form a nanostructures and investigated their electrical and optical properties such as thermal oxidation (Yu and Pan, 2009; Xu et al., 2011); spin coating-pyrolysis method (Sahoo et al., 2010; Farag et al., 2011); chemical vapor deposition (Chien et al., 2010); chemical bath deposition (Chiu and Huang, 2012); sputtering (Sun and Kang, 2010); thermal evaporation deposition (Cheng et al., 2007); sol–gel process with assisted ZnO seed layer (Zhang, 2010). In recent years, ZnO films were synthesized by electrochemical deposition technique (Elias et al., 2008; Hames et al., 2010; Yang et al., 2010).

Cluster-assembled ZnO is one structure which is also interesting and important because of its various fundamental applications in optoelectronic devices, having narrow size distribution between 1 to 10 nm. This attributes to intriguing electronic state and optical

*Corresponding author. E-mail: sutthipoj.s@ku.ac.th.

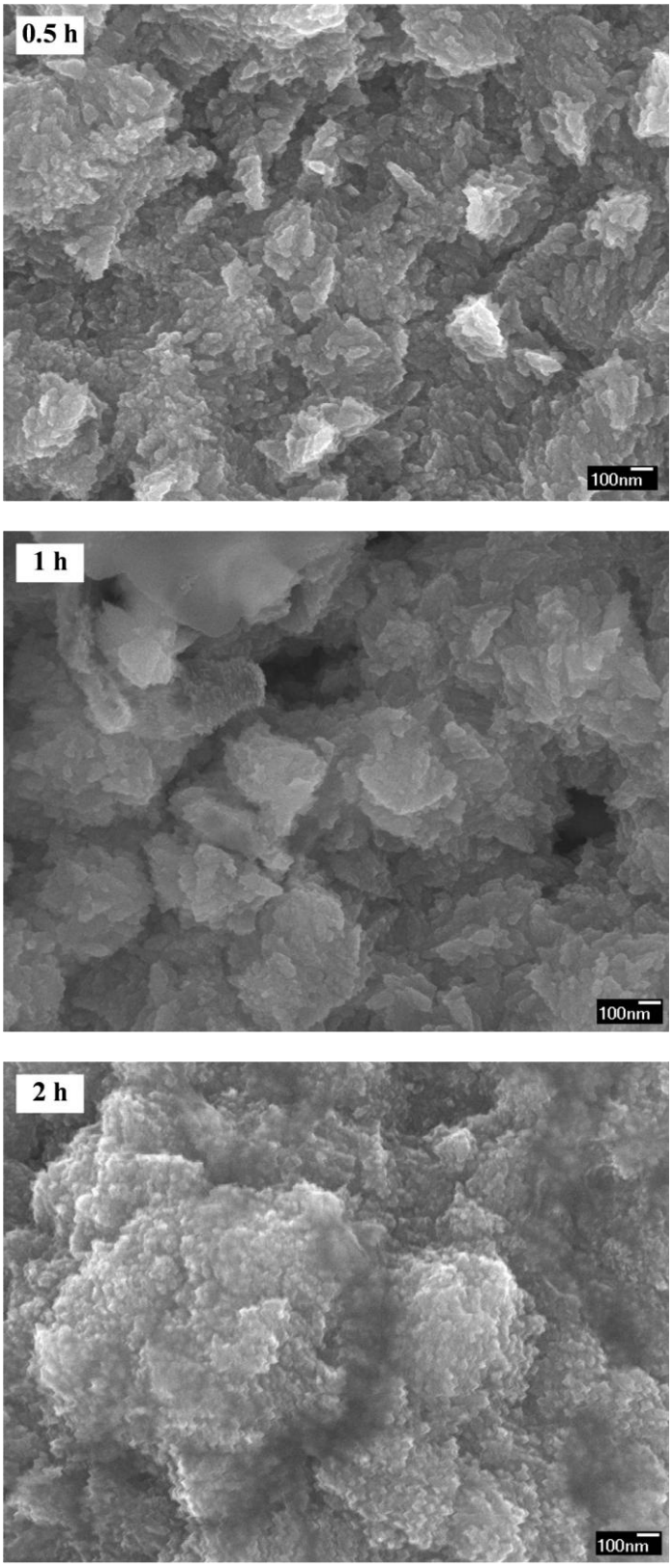

Figure 1. FE-SEM micrographs of cluster-assembled ZnO films on a copper substrate with various reaction times.

properties than bulk material (Zou and Volkov, 1999). Therefore, ZnO nanocluster films with ease to synthesize and low-cost fabrication are both of interest and fundamental technological importance. To understanding the growth mechanism of cluster-assembled ZnO films on copper substrate (Huang and Yuan, 2012), using an electrochemical deposition technique with various reaction time, this technique is demonstrated to prepare ZnO by applying a high electric field. Room temperature is a chosen parameter for deposition of clustered ZnO films on copper substrate. The predomination of this deposition technique is ease to synthesize without the high temperature treatment, simplicity to control the condition of experimental process and also low-cost solution-based deposition process.

MATERIALS AND METHODS

Cluster-assembled ZnO films were prepared by electrochemical deposition on copper substrate (Lin et al., 2011) at room temperature. Zinc nitrate solution was used as a precursor by dissolving 0.025 M zinc nitrate hexahydrate [$Zn(NO_2)_3.6H_2O$] in de-ionized (DI) water, as previously reported (You et al., 2010). Copper substrate was prepared with active area of 1×2 cm^2, cleaned by ultrasonic in de-ionized water, ethanol and acetone for 1 h each, respectively. The reaction process was applied under the stabilized high electric field of 4 kV/m (Buttard et al., 2011) and kept constant for various reaction times of 0.5, 1 and 2 h. Then, all samples were rinsed thoroughly with de-ionized water and dried at 80°C for 24 h in air. The characteristics of morphology of ZnO films in each reaction times were monitored using field emission scanning electron microscopy (FE-SEM), the chemical species composition were investigated by energy dispersive x-ray spectroscopy (EDS) and the crystal structure were examined by x-ray diffraction (XRD).

RESULTS

Figure 1 shows the FE-SEM micrographs of samples with various reaction times of 0.5, 1 and 2 h. It was found that the surface morphologies of ZnO films in various reaction times were formed to be the clustered-like structures. The solution precursor used to form the cluster-assembled ZnO films can be explained in a series of multi-step reactions from the dehydration of zinc nitrate as the following reaction equations (You, 2010):

$$Zn(NO_3)_2 \leftrightarrow Zn^{2+} + 2NO_3^- \quad (1)$$

$$NO_3^- + H_2O + 2e^- \leftrightarrow NO_2^- + 2OH^- \quad (2)$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \leftrightarrow ZnO + H_2O \quad (3)$$

$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \quad (4)$$

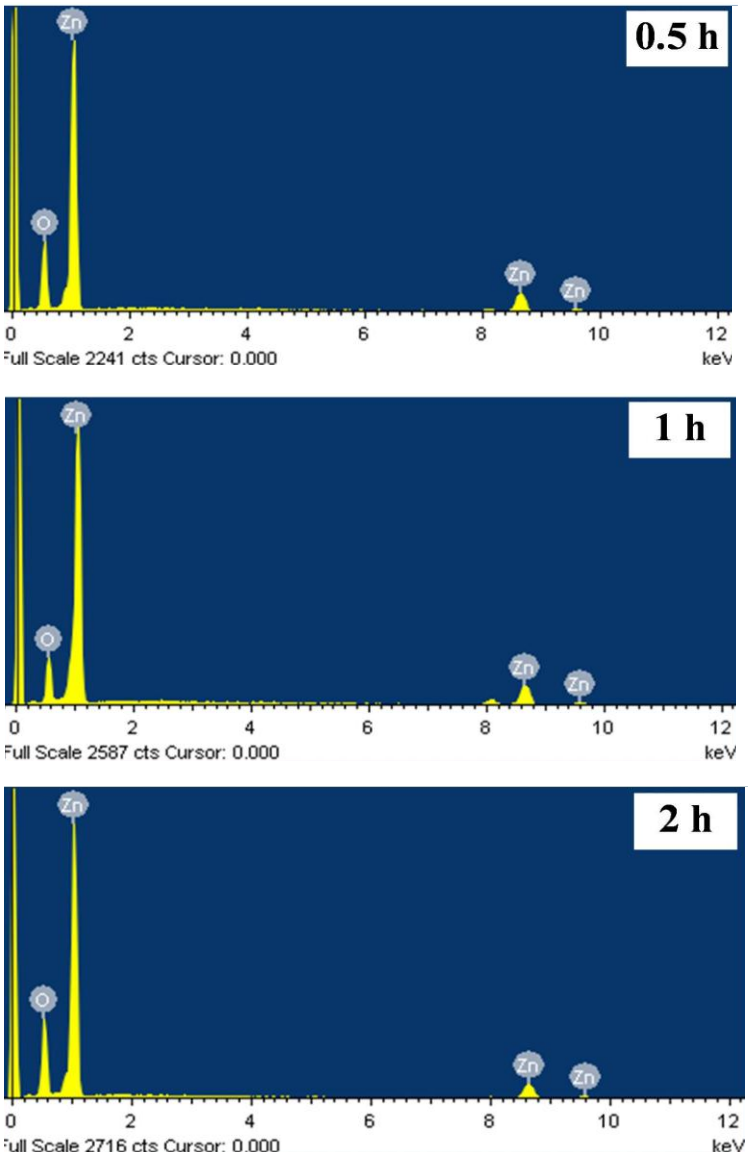

Figure 2. EDS spectra of cluster-assembled ZnO films on copper substrate with various reaction times.

Based on the reaction equation, the stabilized electric field of 4 kV/m was applied in the experiment. The formation of ZnO is reacted between Zn^{2+} ions from Equation 1 and hydroxide anion, OH^- from Equation 2 to form a non-equilibrium $Zn(OH)_2$ immediately in Equation 3. In the final step, the $Zn(OH)_2$ oxidized to form stabilized ZnO crystallites on the copper substrate is given in Equation 4. Instantly, H_2O was produced from the reaction process, leading to reduce the concentration of precursor solution in Equation 1. The clustered structures with formed small grain boundaries were observed for a short time until 2 h of the process, implied that a longer reaction time within 2-h can produce a larger ZnO species and obtain more nascent nanoparticles to form a robust cluster on the substrate. Thus, the reaction time was directly affected to crystal characteristics. Consequently, when the reaction time continually exceeded 2 h, the solution become clear and has some residuals precipitated at the bottom of a beaker, leads to reducing the reaction process and reaction rate was slowed and weakened to grow the nascent ZnO nanoparticles.

Figure 2 showed the energy dispersive x-ray spectra that were monitored using a spot of electron beam on the cluster-assembled ZnO films to investigate the composition. The weight percent ratio of two elements

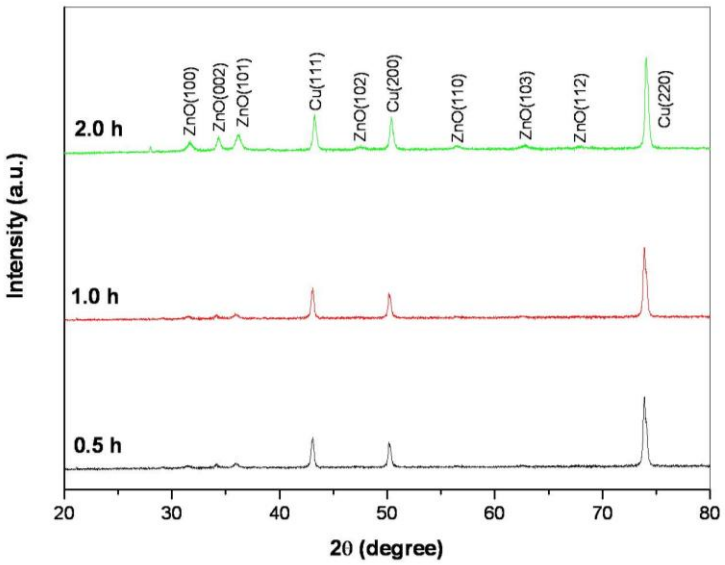

Figure 3. XRD patterns of cluster-assembled ZnO films on a copper substrate with various reaction times.

ranging from 70 to 80 and 20 to 30 wt% for Zn and O, respectively. The XRD measurement was carried out to investigate the structure of the cluster-assembled ZnO films using a wide x-ray beam. The crystal structure of the cluster-assembled ZnO films has been examined by XRD as show in Figure 3. The diffraction peaks at 2θ = 31.8, 34.4, 36.2, 47.5, 56.6 and 62.9° were corresponded to the diffraction patterns of the 100, 002, 101, 102, 110 and 103 planes, respectively. Meanwhile, the diffraction pattern for the first-three peaks consists of 100, 002 and 101 at the reaction time of 2 h are more dominant intensity than other reaction times. It is also obvious that ZnO quantity increases with increasing of reaction time; attributing to the large amount of nascent ZnO nanoparticles formed to larger aggregated clusters on the substrate. A face-centered cubic of copper (Cu) is incorporated in XRD patterns indicating the Cu substrate at 2θ = 43.3, 50.4 and 74.1°, which is consistent peak with 111, 200 and 220 (JCPDS no. 85 to 1326), respectively.

DISCUSSION

The larger grain size are voided in the FE-SEM micrographs after the longer reaction time due to small grain boundaries of the deposited material have coalesced with the cohesive force between particles and being accumulated as non-uniformity clustered ZnO films on copper substrate. Formation of clustered-like structures due to the growth rate of grain is greater than the nucleation rate (Kou et al., 2011). It can be noted that the growth of ZnO films with quality of morphologies and grain sizes via electrochemical deposition can be mainly caused by the optimum reaction time. Presently, the 2 h was the maximum reaction time for the synthesis of nascent ZnO nanoparitcles, formed the cluster-assembled ZnO films due to a longer nucleation time. The EDS spectra of various reaction times from Figure 2 showed a high purity of ZnO films, cluster-assembled ZnO films are composed of Zn and O. It is confirmed that chemical reaction of solution precursor forming as clustered ZnO films on copper substrate without chemical contamination incorporated in the films. It is clearly confirmed by XRD that cluster-assembled ZnO films deposited on copper substrate are the hexagonal wurtzite structures (JCPDS no. 36-1451).

Moreover, quantity of hexagonal wurtzite ZnO films is increased with increasing of reaction time.

CONCLUSIONS

We have successfully synthesized the cluster-assembled ZnO films on copper substrate by electrochemical deposition. The results have been confirmed that the films in each reaction time were incorporated hexagonal wurtzite crystal structures composed of Zn and O. The reaction times were mainly affected to the morphologies of the films. ZnO quantity is increased with longer reaction time. Therefore, synthesis of the hexagonal wurtzite cluster-assembled ZnO films was demonstrated

by electrochemical deposition.

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