Time of Growth Dependent of ZnO-Nanorods by Self-Assembly Methods and its Structural Properties

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Abstract. ZnO-nanorods (ZnO-Nrs) have been successfully prepared on glass substrate using self-assembly method by varying deposition time. Zn acetate dehydrate and 2-methoxyethanol was used as raw material and solvent respectively (for ZnO seed layer preparation), meanwhile Zn nitrate hexahydrate and hexamethylenetetramine (HMTA) dissolved in deionized water used as solution growth of ZnO-Nanorods (ZnO-Nrs). In this work, deposition times of ZnO-Nrs were varied by 120 min, 150 min, 180 min and 210 minutes at 100°C of annealing temperature. In order to investigate the physical properties of resulting ZnO, several measurements such as x-ray diffraction (XRD), ultra-violet visible spectroscopy and scanning electron microscopy (SEM) were carried out. Based on ZnO nanorods SEM image with varying time depositions, seems that increasing deposition time the nanorod size decrease but when the time reach 210 min, the average size of nanorods turned back increase. From XRD measurement, the average grain size and lattice constant (c) which is assemble the nanorod structure and lattice constant (c) was determined by Debye-Scherrer formula and Bragg law’s respectively. The growth process of ZnO nanorod by 180 min time deposition was known as an appropriate time to produce ZnO nanorods with high crystal quality due to sharp peak intensity of XRD spectrum.

1. Introduction

Now days, metal oxide materials have been attractive many researchers according to their semiconductor properties and board application in optoelectronic devices. Titanium dioxide (TiO$_2$), Vanadium oxide (V$_2$O$_5$), Molybdenum trioxide (MoO$_3$) and Zinc Oxide (ZnO) were commonly used in many kinds of electrical devices such as thin film transistor, gas-chemical-biomelecular sensors, light emitting diode, ultraviolet (UV) detector, and solar cells [1]. Besides offer the uniquely properties, the structure of these metal oxides could be easy controlled as needed by using various preparation methods such as vapor based deposition (metal oxide chemical vapour deposition-MOCVD), pulsed laser deposition (PLD), epitaxy and solution-chemical based deposition. Among these methods, the simplest one is using solution-chemical based deposition such as sol-gel method, spray-pyrolysis, hydrothermal, and also self-assembly.

ZnO, one of the semiconducting material, has attracted considerable in optoelectronics field because of its wide bandgap (~ 3.4 eV), wide resistivity range (10$^{-4}$ – 10$^{12}$ Ω.cm) high exciton binding energy (~ 60 meV), and already claimed show a long-term stability [2, 3]. Many variations of ZnO
micro/nano structured have been developed and already reported as photoelectrode in light based devices, particularly in solar cells technology [4]. ZnO nanoparticles as electron transport material in organic or hybrid solar cell has been reported in past ten years [5,6]. Besides that, this metal oxide also generally used in emerging photovoltaic devices, such as perovskite solar cell and dye sensitized solar cells [7,8]. Silicon solar cell technology also use this kind metal oxide as anti-reflectance coatings in order to enhance solar irradiation adsorption by using special nano-structure moth eye facet of ZnO which is shows more than 40% increments on short circuit current and conversion efficiency [9]. The nanostructured of ZnO in photoelectrode or photoanode system for solar cell technology, played an important role in charge carrier collection and drive the recombination rate. The appropriate nanostructures such as nanorod, nanowire, nanocone, nanobelt or even nanoforest of ZnO have been claimed could be increase the solar cell performance according to high efficiency in charge transport and reduce the recombination rate [10].

In general, ZnO-nanorods growth using solution based preparation and thermal treatment has been well reported [11]. Kyung et.al. prepared the ZnO-nanorod structure using chemical solution deposition and shows that the annealing temperature influences the alignment and length of the resulting nanorod. It was also reported that ZnO seed layer properties such as crystallinity, surface morphology, thickness and preparation condition provide high influence on ZnO nanorod growth [3]. In contrary, D. Polsongkram et.al claimed that their procedure by using hydrothermal method allows the growth of ZnO nanorods without any seed and/or surfactant but they also imply that the precursor concentration and deposition time have a big influence on the morphology and ordering ZnO nanorods [12]. In this work, the ZnO with nanorods structure were prepared using an easy and low-cost self-assembly growth technique at certain annealing temperature and variation of deposition time.

2. Experimental Methods

All chemicals used in this study were analytical grade without further purifications. Zinc acetate dehydrate (Zn(CH$_3$COO)$_2$.2H$_2$O) and zinc nitrate hexahydrate(Zn(NO$_3$)$_2$.6H$_2$O) purchased from Merck used as raw material for ZnO seed layer preparation and ZnO nanorods growth solution respectively. Two layers of ZnO seed layer were deposited on glass substrate using spin coating technique at 1500 rpm. Before used glass substrate was cleaned in ethanol and acetone by ultrasonic cleaner equipment. ZnO seed layer precursor made from 0.5 mM zinc acetate dehydrate in 2-methoxyethanol anhydrous (Sigma-Aldrich) and diethanolamine (Sigma Aldrich) as a solvent and stabilizer respectively. A transparent precursor solution was achieved and continued with deposits it onto cleaned glass substrate. Two step annealing treatment at 250°C and 500°C was followed to forming the ZnO particles as seed layer. These all methods following the procedure from our previous research [5].

ZnO nanorods (ZnO-Nrs) were grown by self-assembly method in isolated weighting bottle, with glass substrate/ZnO seed layer side was facing down at 45°. The growth solution was prepared by dissolving equimolar zinc nitrate hexahydrate and hexamethylenetetramine in deionized water. Growth temperature was fix at 100°C for 120 min, 150 min, 180 min and 210 minutes inside the regularly laboratory oven. After that, ZnO nanorods was washed in ethanol and deionized water several times and then annealed at 500°C for 30 min on isolated hotplate.

The scanning electron microscopy (JEOL JSM-6510A) was used to identify the surface morphology of different time of growth ZnO-Nanorods. In order to study the absorption spectrum during deposition time, ultra-violet visible spectroscopy (T70+ PG Instrument) was carried out for each sample. To confirm the nanorod structure, the equipment of X-pert Pro, PW3050/60 x-ray diffractometer was used and continued with data analysis to determine crystals lattice of ZnO-Nrs by Debye-Scherer formula.

3. Results and Discussion

Figure 1 shows the morphology of ZnO-Nanorods (ZnO-Nrs) resulted that prepared with self-assembly method at 100°C annealing temperature by 120 min, 150 min, 180 min, and 210 minutes’ time deposition. Up to 180 min time deposition the average diameter seems decrease but back to
increase at 210 min. It is clear that ZnO forms hexagonal wurtzite but unfortunately the diameter size shows a broad range. For 120 min deposition time the average of diameter size is about 100 nm-200 nm, 150 min is 100 nm-160 nm, 180 min is 80-140 nm and for 210 min is 100 nm-200 nm (figure 3(b)). Although the range of diameter size not significantly differ between each samples this images show that increasing time deposition the surface of ZnO-Nrs growth denser. In figure 1 the lower time deposition (120 min) shows a large empty space compare with 180 min (figure 1 (c)) and 210 min (figure 1(d)) however the hexagonal structure for sample with 210 min time deposition appears to be defected.

![SEM images of ZnO-Nanorods grown on glass substrate by variation growth time during self-assembly deposition](a) 120 minutes (b) 150 minutes (c) 180 minutes and (d) 210 minutes.

To verify the nanorod structure, x-ray diffractometer was used to investigate the structure and the results are shown in figure 2. All diffraction peaks can be indexed to hexagonal wurtzite structure in accordance with JCPDS 36-1451 (Joint Committee on Powder Diffraction Standards) of ZnO ($a = 3.249 \text{Å}, c = 5.206 \text{Å}$). All samples show highly possessed c-axis orientation according to narrower and highly dominant peak at (002). Other peak that attributed to others crystal orientation of ZnO is very small so that the rod structure is dominant. The sharp and narrow diffraction peak indicate that this metal oxide has good crystallinity as shown in figure 2. The peak intensity on XRD spectrum for deposition time up to 180 min was increase in contrast with 210 min, indicating that for the sample with 210 min time deposition the quality crystal was reduce. This situation can be related to the concentration of $[\text{Zn}^{2+}]$ and $[\text{OH}^-]$ during increments of time which is facilitating the supersaturated condition of precursor aqueous solution [12]. When the time increase more than 180 minutes, the condition is over supersaturated thus the existence of separated clusters Zn(OH)$_2$ were run out and the longer time in deposition process will deteriorates crystal structure growth.

Figure 1. Scanning electron microscope (SEM) images of ZnO-Nanorods grown on glass substrate by variation growth time during self-assembly deposition (a). 120 minutes (b) 150 minutes (c) 180 minutes and (d) 210 minutes.
Figure 2. XRD spectra of zinc oxide nanorods layer on glass substrate by variations deposition time. All peaks were agreeing with JCPDS data for hexagonal wurtzite zinc oxide structure. A dominant (002) preferred orientation was appeared as time of growth increase. Particularly for samples up to 180 min growing time. Indicates that there was an optimum time for deposit nanorod structure at certain precursor concentration.

The defect on crystal growth at 210 minutes of deposition time, clearly seen at figure 2, all peaks position for this sample were shifted approximately 0.1°-0.4° compared with JCPDS ZnO data. Table 1 shows the XRD data from the JCPDS card compared with the XRD ZnO results. The average grain size can be simply determined using Scherrer’s formula and already reported elsewhere [13]:

$$D = \frac{k \lambda}{B \cos \theta}$$  \hspace{1cm} (1)

where $k$ is the Scherrer constant, which is dependent on the crystallite shape and can be considered as 0.9 [14]; the x-ray wavelength of the incident Cu Ka radiation ($\lambda$) is 0.154 nm; $B$ is the FWHM (full width at half maximum) of the respective peak; and $\theta$ is diffraction peak angle at certain plane. The calculated crystallite (grain) size is presented in table 1. The result showed that the ZnO-Nrs grain size tend to be decrease as time deposition increase. The ZnO particle nucleation process was beginning when the solution is supersaturated and continued to merge each other to form ZnO structures [12]. An appropriate time deposition will facilitate the supersaturation solution and produce a higher crystals quality (shows with sharp peak intensity on XRD spectrum) and smaller grain size (decreased FWHM) [3]. Smaller grain size was also caused by the ZnO molecule at the surface are energetically less stable, thus a longer deposition time was estimated to produces ZnO-Nanorods with high aspect ratio (ratio between length and diameter of ZnO) [12]. The lattice constant $a$ and $c$ of the ZnO wurtzite structure can be measured using Bragg’s law [13]:

$$a = \frac{1}{\sqrt{3}} \frac{\lambda}{\sin \theta}$$  \hspace{1cm} (2)

$$c = \frac{\lambda}{\sin \theta}$$  \hspace{1cm} (3)

Unfortunately, the lattice constant $a$ cannot be directly calculated using equation (2) because the peak of (100) plane does not appeared for all samples in XRD spectra. This situation may be related to the growth ZnO-Nrs behavior in this case.
Table 1. XRD parameter of ZnO-Nrs

| Crystal plane | (002) | (101) | (102) | (103) |
|---------------|-------|-------|-------|-------|
| Deposition time | D (nm) | c (Å) | 2θ (°) |       |
| 120           | 24.8  | 5.18  | 34.61 | 36.37 | 47.77 | 63.05 |
| 150           | 25.6  | 5.20  | 34.49 | 36.27 | 47.61 | 62.89 |
| 180           | 22.1  | 5.19  | 34.52 | 36.41 | 47.63 | 62.97 |
| 210           | 16.0  | 5.14  | 34.85 | 36.69 | 47.97 | 63.25 |
| JCPDS         | -     | 5.20  | 34.42 | 36.25 | 47.53 | 62.86 |

Figure 3. (a) Ultraviolet (UV) visible spectra of ZnO-Nanorods layers with variation of deposition time. (b) Graph of deposition time versus average diameter ZnO nanorod.

Figure 3(a) represent the result of ultra violet (UV) visible spectroscopy characterization in the wavelength range of 300 – 750 nm for each sample, including ZnO seed layer. The result shows that during time deposition increases the absorbance increased, except for the sample with 210 minutes time deposition. This situation can be explained by increments time of growth at certain concentration and temperature while the colloidal suspension of the precursor has been over supersaturated, the crystal growth was stopped/freezers and discontinue the altitude growth and the quantity of ZnO crystallite/grain. The absorbance spectrum of ZnO seed layer exhibit strong exitonic absorption peak at 360 nm and high transparency (>95%) at visible range. This seed layer is critical point for growing ZnO nanorod structure as mentioned by H.J. Lee et.al whose reported that the lack quality of seed layer can results the randomly oriented of ZnO nanorod [15].

4. Conclusions
In this study, the effect of time deposition for growing ZnO nanorod structure was investigated. From the experimental results, it can conclude that deposition of ZnO-Nrs on ZnO seed layer/glass substrate using self-assembly method at 100 °C deposition temperature, has limited time on deposition process (approximate at 180 minutes’). From SEM images, increasing time deposition also reducing the average diameter size of nanorods as shown in Fig.3(b), but when the time is over than 180 min in this case at 210 minutes; the rod diameter seems back increase. XRD measurement reveal that the grain size of ZnO nanorods tend to reduce as time deposition increase. All samples exhibit preferred orientation along c-axis (002) plane with sharp and narrow peak while other peaks have low intensity, indicate that crystal structure at (002) plane has good crystal quality in the other words it has been present a rod structure. The transparency of ZnO nanorods is decrease for all samples up to 180 minutes’ time deposition related to quantity of ZnO-Nrs. Unfortunately, the aspect ratio (L/r; length/radius) of nanorod structure cannot be estimated because the lack of data nanorod length (cross-sectional SEM images).
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