Influences of Al dopant atoms to the structure and morphology of Al doped ZnO nanorod thin film

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Abstract. We report our work about dependency of Al dopant atoms to the growth process of Al doped ZnO (AZO) nanorod structure. ZnO is one of type metal oxide, which is classified as semiconducting material with direct wide band gap (~ 3.4 eV). This metal oxide is widely used in optoelectronic devices, such as solar cell, gas sensing, and photocatalyst. To produce effective photoelectrode in solar cell devices and high sensitive sensor in gas sensing application, many researchers have been modifying the nanostructure, such as inserting dopant ions, variation in deposition technique and surface modifications. By inserting some dopant ions/atoms, the structure and morphology of ZnO nanorod can be controlled. Nucleation process of nanorod structure which is growth by chemical solution method, are depend on seed layer morphology. We have prepared ZnO nanorod thin film (growth by self-assembly method) with inserting aluminum as dopant atom both in seed layer and nanorod growth solution. The morphology of ZnO nanostructured significantly changes as the existence of aluminum atoms. Based on X-ray diffraction pattern, the wurtzite structures of AZO nanorod still possessed and only affect to the small shift of lattice crystal. A high surface roughness of seed layer can produce wide radius of nanorod, since the nucleation process initiated by seed layer particle size as a template of nanorod arrangement.

1. Introduction

Nanostructured of semiconducting material possess convenient and useful in physical, electrical, and optoelectronic properties in accordance with device applications. For emerging photovoltaic devices, ZnO photoanodes with variety of nanostructures have been confirmed can increase solar cell performance [1, 2]. ZnO ‘trees like’ structure called as nanoforest, with high density and long branched hierarchical crystalline phase could significantly improve the efficiency of DSSC (dye sensitized solar cell) [2]. This specific structure can increase the photogenerated current due to greatly augmented surface area supporting higher dye loading and light harvesting. An appropriate nanostructured can reduce the charge recombination through direct conduction along nano-crystalline ZnO. Feng Xu et.al have been synthesised ZnO nanoarchitectures with two-step process and produced nanowire-nanosheet assembly which is increases power conversion nearly twice as high as that of the DSSC using the primary ZnO nanosheet arrays [3].
In other electronic devices such as gas sensing, ZnO was widely used as an active component to detect the existence some toxic gases [4]. Compared to TiO₂, ZnO shows a good catalytic reaction in the gas sensor due to existing various defects such as oxygen vacancies, zinc interstitials, and oxygen interstitials. The performances Gas sensor-based metal oxides can be enhanced by modifying the morphology that increasing the surface-to-volume ratio, creating more centres for gas interaction, and changing the energy band structures [5]. One of effort in modifying ZnO structure is by inserting dopant ions/atoms [4]. Some literatures have reported that Al doping can increase the sensitivity and conductivity of ZnO respects to accelerating chemical reactions in the gas sensor [4]. Moreover, Al doped ZnO based materials such as ZnAl₂O₄ is also suitable for ultraviolet electronic applications for the example is photocatalyst [6].

A low surface roughness of ZnO seed layer shows tendency to produce smaller diameter of ZnO nanorod [7]. In this work, we studied the existences of aluminum content to the ZnO structure. In order to observe the influence of aluminum dopant to the formation of AZO nanorod structure, aluminum chloride as doping agent was inserted in precursor solution of ZnO seed layer and nano-rod growth. Intercalation of aluminum atom to ZnO nanorod structure was estimated occurred during deposition processes via self-assembly.

2. Experimental Methods
All chemicals used for preparation both of Al doped ZnO seed layer and nanorod thin film were analytical grade without further purifications. As the purposes for optoelectronic device applications, Al doped ZnO nanorod was deposited on FTO (fluorine doped tin oxide) substrate. Before used FTO substrates were cleaned and washed by ethanol and acetone in ultrasonic bath. 0.5 mM Zinc acetate dehydrate (Zn(CH₂COO)₂.2H₂O-Merck) in 2-methoxyethanol and diethanolamine (Sigma-Aldrich) as stabilizer was used as precursor of ZnO seed layer (ZnO-SL). Aluminum chloride (Sigma-Aldrich) (0.5 wt%) was added for inserting dopant atoms in ZnO-SL. ZnO-SL was deposited on cleaned FTO substrate by spin coating method. The preparation of Al doped ZnO seed layer was followed our previous work [7, 8].

Undoped ZnO and Al doped ZnO nanorods (ZnO-Nrs) were grown by self-assembly method in isolated glass bottle. The Al doped ZnO seed layer on FTO substrate (FTO/Zn-SL) was positioned facing down at 45° inside glass bottle. The solution for growing ZnO nanorods was prepared by dissolving equimolar zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O-Merck) and hexamethylenetetramine in deionized water [9]. 0.5 wt% and 1 wt% of Aluminum chloride respect to the zinc nitrate hexahydrate was added for inserting Al dopant atoms on the growth process. Growing temperature was fixed at 100°C for 150 min inside the regularly laboratory oven. After that, the resulted undoped ZnO (0-0 wt%) and Al doped ZnO nanorods thin film was washed in ethanol and deionized water several times and subsequently annealed up to 500°C for 30 minutes on isolated hotplate.

The influences of Al dopant ion to the both of ZnO seed layer and nanorod optical properties were also investigated using UV-Vis spectroscopy. Structure and morphology of Al doped ZnO thin film were observed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The grain crystal size of Al doped ZnO thin films were calculated using Debye Scherer equation. To ensure the nanorod morphology, tunneling electron microscope (TEM) was also carried out.

3. Results and Discussion
The ultraviolet visible (UV-Vis) absorbance spectra of Al doped ZnO nanorod thin film is shown in figure 1 ZnO seed layer (ZnO-SL) has highly transparent in visible wavelength and shows UV absorbance peak at 367 nm. Among the other samples, undoped ZnO nanorod (ZnO-Nr) thin film has highest UV absorbance peak which identified at 378 nm. The sample with Al dopant atoms (0.5 wt%) both in seed layer and nanorod growth solution is denoted by AZO-Nr 0.5-0.5. Whereas, AZO-Nr 0-0.5 is use undoped ZnO thin film as seed layer whilst employing 0.5 wt% Al in nanorod growth solutions. The Al atoms in AZO-Nr thin films can reduce the absorbance spectrum in visible wavelength although there is a small increment at 400-470 nm (for AZO-Nr 0.5-0.5). AZO-Nr thin
film relatively shows high transparency compared to ZnO-Nr in visible wavelength relates to the smaller nanorod size. The secondary absorbance peaks below 370 nm which are identified for both of AZO-Nr thin films, were estimated relates by the existences of smaller size of ZnO. The smaller particles can decrease the onset absorbance curve due to quantum confinement size effects [10]. The influence of inserting Al dopant in ZnO particles is already report in many references [11]. Aluminium atom has been proved can reduce ZnO particle size which affect the optical properties, such as absorbance/transmittance and also photoluminescence [12]. The size reduction was played by Al atoms which has smaller atomic radius (~118 pm) compared than Zn (142 pm); that occupy the Zn sites (Zn vacancy) [13]. The identification of reduction particle size and the changes of ZnO structure by Al dopant are also clarified by SEM image and XRD results respectively, which are shown in figure 2 and 3.

![Absorbance spectra of undoped ZnO nanorod, Aluminum doped ZnO nanorod (AZO-Nr), and ZnO seed layer (ZnO-SL) thin films.](image)

**Figure 1.** Absorbance spectra of undoped ZnO nanorod, Aluminum doped ZnO nanorod (AZO-Nr), and ZnO seed layer (ZnO-SL) thin films.

The influence of Al dopant to the morphology of ZnO nanorod was observed by scanning electron microscopy (SEM) that shown in figure 2. The surface and cross section morphology of each layer are provided in the figure. All samples present vertically aligned hexagonal rods structure. The diameter are varied and relate to the existences of Al dopant. The rod diameter is significant depend on the existences of Aluminum dopant. Undoped ZnO-Nr has a largest diameter (~ 450 nm) whilst all of samples AZO-Nrs have varied size which is not show significant different from each other (40 ~ 130 nm). The different result between AZO-Nrs thin film are identified in rod well alignment and empty space between rods on each sample. Al dopant is not only affects the rod diameter \(d = 2r\) but is also effect to the length \(L\). Inserting 0.5wt% of Al dopant both in seed layer and growth solution will reduce significantly the length of rod structure. Subsistence of Al atoms can increase the aspect ratio \((L/r)\) of ZnO nanorod structure [14]. The table 1 shows aspect ratio comparison of all samples. Higher aspect ratio is obtained by 0.5-0.5 wt% which is imply that aluminium atom shows tendency to reduce in diameter rather than length of rod structure.
Figure 2. SEM images of ZnO-Nr and AZO-Nr thin film. (a) - (b) ZnO-Nr [7], (c) - (d) AZO-Nr (0-0.5), (d) - (e) AZO-Nr 0.5-0, (g) - (h) AZO-Nr 0.5-0.5.

Figure 3 shows X-ray diffraction pattern results of ZnO-Nr and aluminium doped ZnO (AZO-Nr). All samples show hexagonal wurtzite structure with c-axis (002) plane preferred orientation. Surprisingly, the (101) plane of metallic zinc are identified in each sample ($2\theta \equiv 43^\circ$). It is probably relate to the existence and agglomeration of Zn-interstitial in all samples during growing process and
annealing treatment. Debye-Scherer formula was used to determine crystal size using the full width at half maximum (FWHM) of the strongest (002) diffraction peaks. The resulting calculation of average crystallite size is tabulated in table 2. Seed layer morphology was play an important role to control crystal size of ZnO [15]. The used of undoped ZnO seed layer (0-0 wt%) produced a largest crystal size among the others. The small grain size of seed layer tends to be produced relatively small diameter of rod and vice versa. To ensure the morphology of rod structure, the exfoliated thin film of AZO-Nrs 0.5-0.5 was observed by TEM (tunneling electron microscopy) as presented in figure 4. Although AZO-Nr seems overlap but the size and morphology of rod structure are clearly identified.

![Figure 3. X-ray diffraction pattern of ZnO-Nr and Al doped ZnO (AZO-Nr).](image)

Table 1. Aspect ratio (L/r) of ZnO and Azo-Nrs. The length (L) and diameter (2r) of nanorod were obtained from SEM images.

| Aluminum Content | Length (μm) | Radius (μm) | Aspect Ratio (L/r) |
|------------------|-------------|-------------|-------------------|
| Seed layer – nanorod |             |             |                   |
| Undoped (0-0 wt%) | 2.63        | 0.225       | 11.69             |
| 0.5-0 wt%        | 1.95        | 0.07        | 27.86             |
| 0-0.5 wt%        | 1.05        | 0.065       | 16.15             |
| 0.5-0.5 wt%      | 1.7         | 0.06        | 28.33             |
Table 2. Comparison of crystal lattice and crystallite size of ZnO-Nr and AZO-Nr.

| Aluminum Content inside ZnO SL-ZnO Nanorods | 2\text{\textdegree} (002) | c (Å) | D (nm) |
|---------------------------------------------|---------------------------|-------|--------|
| 0-0 wt %                                    | 34.226                    | 5.24  | 105.13 |
| 0.5-0 wt%                                   | 34.258                    | 5.23  | 71.39  |
| 0-0.5 wt%                                   | 34.215                    | 5.24  | 86.27  |
| 0.5-0.5 wt%                                 | 34.235                    | 5.23  | 68.39  |

ZnO (JCPDS) 34.42 5.2 -

Figure 4. Tunneling electron microscopy (TEM) image for exfoliated of AZO-Nr (0.5-0.5) thin film. The rod structure clearly identified with a diameter approximately of ~80 nm and length of around 300 nm and 650 nm.

4. Conclusions
In summary, aligned growth of ZnO and Al doped ZnO nanorods have been successfully prepared on FTO substrates using self-assembly method. The inserting of aluminum dopant (0.5 wt%) in seed layer and nanorod growth solution have been proved can reduce significantly the nanorod size (both of diameter and length). The existences of Al in seed layer, can reduce the surface morphology due to reducing ZnO particle size. As initiator layer, grain size of seed layer is strongly affect the nanorod growth. The smallest crystal size and largest aspect ratio (28.33) is obtained by AZO-Nrs 0.5-0.5. This situation can be explained by an occupying aluminum atom at Zinc sites in rod structure which is reducing the nanorod size. Aluminum has a smaller atomic radius (118 pm) compare with Zn atom (142 pm). Nevertheless, in this case the Al substance likely tendency to produce random rod aligned due to smaller formed rods.

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