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SYNTHESIS OF ZnO NANOROD ARRAYS ON ZnO NANOPARTICLES-COATED ITO SUBSTRATE

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ABSTRACT

ZnO nanorod arrays have been grown on ITO glass substrates which were pre-coated with ZnO nanoparticles by using a low cost and low temperature chemical solution method. The structural and optical properties of ZnO nanorod arrays were investigated using scanning electron microscopy (SEM) and photoluminescence (PL) techniques. It was demonstrated that the introduction of annealed ZnO nanoparticles seed layer is required for the formation of well-aligned ZnO nanorods. The ZnO nanorod arrays with a diameter of 40-70 nm and a length of 200-300 nm were obtained. Besides, a strong UV emission peaked at 386 nm in the PL spectrum revealed the good crystal quality of ZnO nanorods.

INTRODUCTION

One-dimensional (1-D) semiconductor nanomaterials have been attracting increasing attention due to their outstanding properties, which are different from bulk materials. Particularly, well-aligned ZnO nanorod arrays show great potential for solar cell application [1-2]. In the past years the number of ZnO nanorod arrays synthesis techniques, including vapour–liquid–solid (VLS) growth [3], chemical vapour deposition (CVD) [4], electrochemical deposition [5], and chemical solution method [6-8], has grown exponentially. The chemical solution approach is considered the most promising technique to grow ZnO nanorod arrays due to its simplicity and economical for large scale preparation of ZnO nanorod arrays.

In the present work, the synthesis of ZnO nanorod arrays using chemical solution approach is described. It was found that ZnO nanorod arrays could only be formed on annealed ZnO seed layer, but not on the bare ITO substrate and unannealed ZnO seed layer. The ZnO nanorod arrays with a diameter of 40-70 nm and a length of 200-300 nm were successfully produced on seeded-ITO substrate.

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EXPERIMENTAL METHOD

0.3 M zinc acetate dihydrate was first dissolved in ethanol. For total dissolution, equal molar amount of diethanolamine was added slowly to the solution. The resultant solution was stirred at 60 ^{o}C for 30 min to yield a clear transparent homogeneous solution. After aging for 24 h, the solution was subjected to spin coating on the ITO-coated glass substrates. The ITO-coated glass substrates were cleaned ultrasonically in 2-propanol and acetone for 15 min each. The solution was spin-coated onto ITO-coated glass substrates with a spinning speed and time of 2000 rpm and 30 s for three times. After each coating, the samples were dried at 100 ^{o}C for 10 min in air. Finally, the samples were annealed at 300 ^{o}C for 1 h in air to obtain ZnO nanoparticles seed layer.

ZnO nanorods were grown on the seeded-substrates by immersing them in a closed vial containing 25 mM zinc nitrate hexahydrate and 25 mM hexamethylenetetramine (HMT) in deionized water at 60 ^{o}C for 4 h. For comparison, ZnO nanorods were also grown on the bare ITO substrates and unannealed ZnO seed layer. Subsequently, the substrates were rinsed thoroughly with DI water to remove any residual reactants and dried in air at 100 ^{o}C for 10 min.

Scanning electron microscopy (SEM) (1450VP, LEO) and energy-dispersive X-ray spectroscopy (EDS) attached to the SEM were used to investigate the morphology and composition of the as-grown ZnO nanorods. Besides, to exclude the PL emission from ITO, the PL property of nanorods grown on seeded-quartz substrate at room temperature was investigated using Perkin Elmer LS55 Luminescence Spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the ZnO seed layer annealed at 300 ^{o}C with a particle size of 10-20 nm deposited on the ITO substrate. After chemical solution growth, a dense array of hexagonal ZnO nanorods having a diameter from 40 nm to 70 nm was formed as shown in Figure 2a. The cross-section image of ZnO nanorod arrays is shown in Figure 2b. It was found that all ZnO nanorods grew almost perpendicularly to the seeded-substrate, and the length of ZnO nanorods is about 200-300 nm.

To elucidate the role played by ZnO seed layer, the ZnO nanorods grown on bare ITO substrate under the same experimental condition are shown in Figure 3a. It is seen from the SEM image that the ZnO rods with much larger size were distributed randomly over the whole substrate surface. Besides, the SEM image of ZnO nanorods grown directly on unannealed ZnO seed layer was also given in Figure 3b. Without the annealing process, ZnO nanorod arrays did not grow, but resulting in the formation of randomly distributed ZnO rods. This result indicated that the zinc acetate crystallites only decompose after annealing and ZnO nanoparticles which are surface active and well-oriented with (002) planes parallel to the substrate form. According to previous work [7], the introduction of a well-oriented ZnO seed layer on the substrate is the main factor in controlling the alignment of ZnO nanorods.

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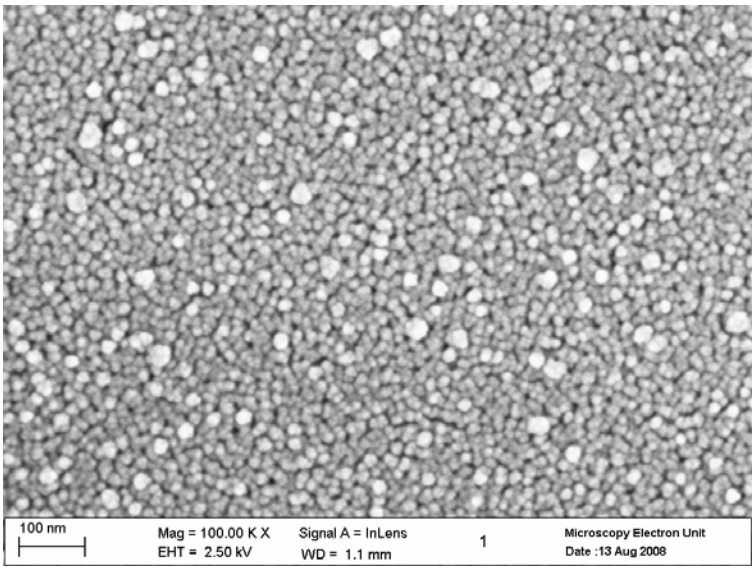
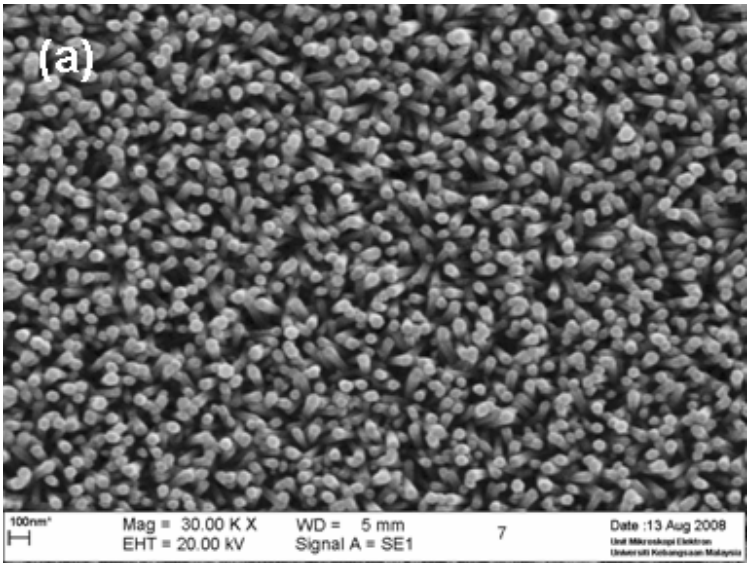


Figure 1: SEM images of ZnO seed layer annealed at 300 ^{o}C



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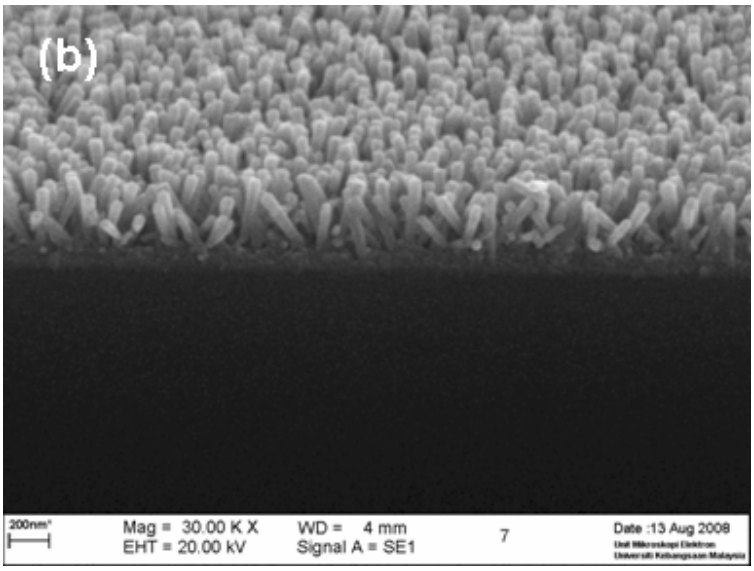
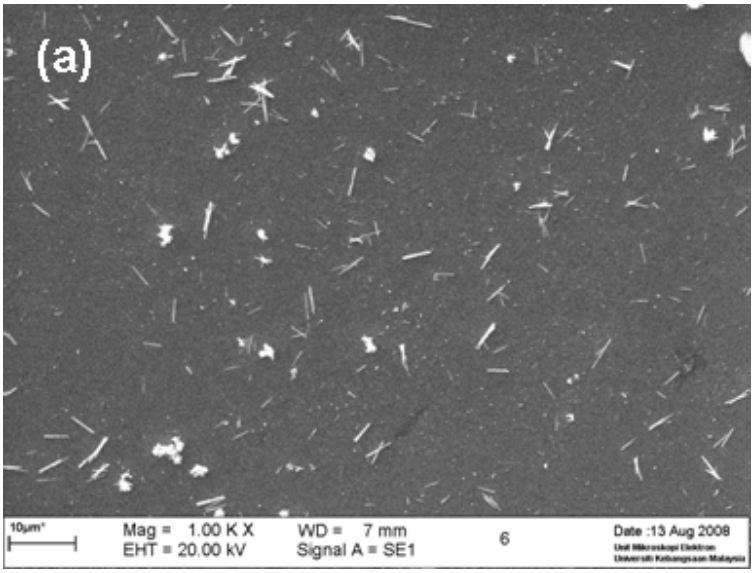


Figure 2: a) Top-view and b) cross-sectional SEM images of ZnO nanorod arrays grown on seeded-ITO substrate



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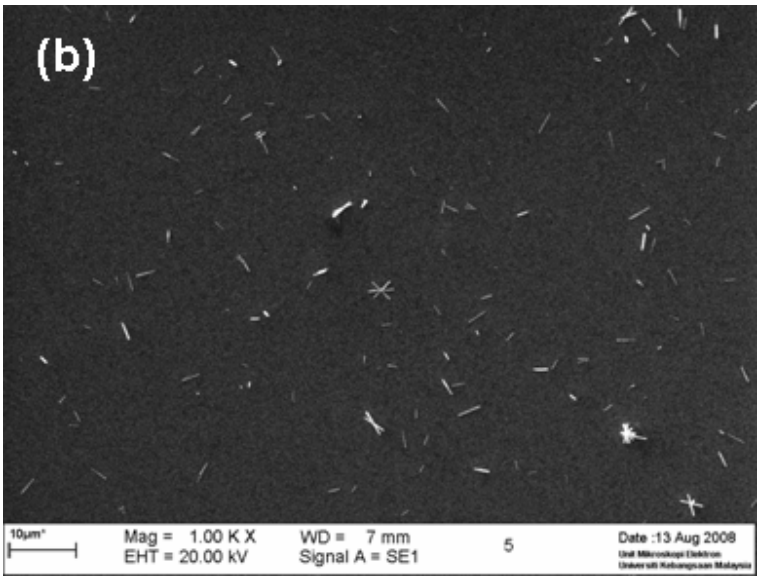

Figure 3: SEM images of ZnO rods formed on (a) ITO substrate and (b) unannealed ZnO seed layer.

To check the chemical composition of the as-grown ZnO nanorods, an energy-dispersive X-ray (EDX) spectrometry analysis was performed. Figure 4 shows a typical EDX spectrum of ZnO nanorod arrays grown on seeded-quartz substrate. Three main peaks have been clearly observed from the spectrum, which are related to zinc, oxygen and silicon. The presence of the silicon peak in the spectrum was due to the quartz substrate. Besides, only Zn and O were detected from the sample, confirming the composition of ZnO nanorods. However, the atomic composition ratio of O to Zn could not be determined since a portion of O originated from the quartz substrates.

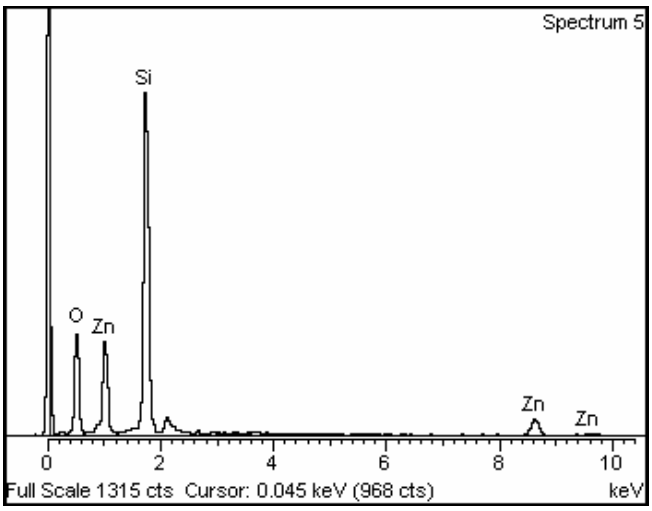

Figure 4: EDX spectrum of the ZnO nanorods grown on seeded-quartz substrate

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To exclude the influence from the ZnO film, PL spectrum of the ZnO seed layer was also measured. Figures 5 compares the room temperature PL spectra of the ZnO seed layer and ZnO nanorod arrays. At the same excitation power, the PL intensity of the ZnO seed layer was negligible in comparison with that of the ZnO nanorod arrays. The PL spectrum of ZnO nanorods grown on ZnO-seeded quartz substrate, recorded by using an excitation wavelength of 325 nm at room temperature, showed a characteristic narrowband at 386 nm (Figure 5). Normally ZnO nanostructures can exhibit UV emission resulting from the recombination of free excitons [9] and visible emissions (defect emissions) due to some structural defects [10-11], respectively. The strong UV emission in the PL spectra indicated that the ZnO nanorods had a good crystal quality with few oxygen vacancies.

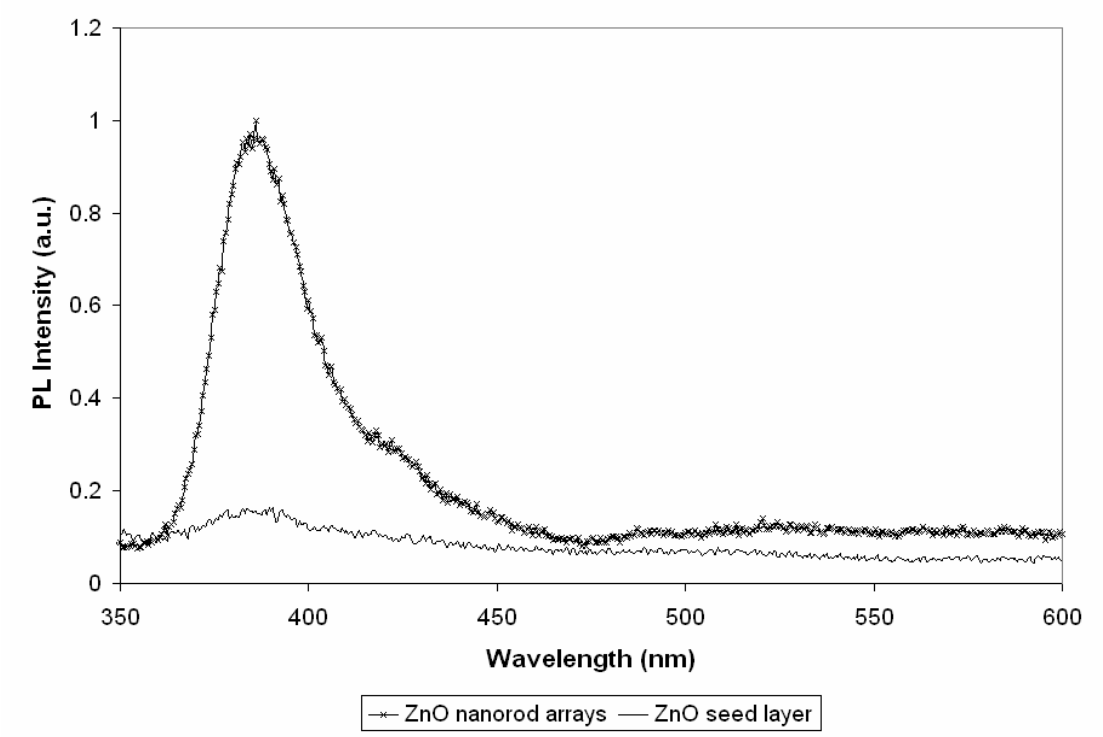

Figure 5: Room temperature photoluminescence spectra of ZnO nanorod arrays and ZnO seed layer

ZnO nanorods were grown in aqueous solution of zinc nitrate hexahydrate and HMT. The growth of oxide nanorods from aqueous solution involves controlled precipitation on a substrate through hydrolysis/condensation reactions of metal ions and their complexes. In our chemical solution, the HMT decomposed to formaldehyde (HCHO) and ammonia (NH_3), which acted as a PH buffer and supply of OH- slowly. The following reactions were involved in the crystal growth of ZnO nanorods [12]:

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$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$2OH^- + Zn^{2+} \rightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

ZnO seed layer served as nucleation sites and also provided a preferential crystallographic growth direction to the resulting nanorods. Due to the polar nature of (0 0 1) plane, ZnO surface is charged positively or negatively easily. Then the surface attracts ions of opposite charges (OH^- or Zn^{2+}) and this new surface in turn attract ions with opposite charges to cover the surface next and thereby reacting to form ZnO [8].

CONCLUSION

The synthesis of ZnO nanorod arrays using chemical solution approach has been demonstrated in this work. ZnO nanorods arrays were not formed on the bare ITO substrate and unannealed ZnO seed layer. The annealed ZnO seed layer was required for the growth of well-aligned ZnO nanorod arrays on the substrates. The ZnO nanorod arrays with a diameter of 40-70 nm and a length of 200-300 nm were successfully synthesized.

ACKNOWLEDGMENT

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