Synthesis of ZnO Micro Prisms on Glass Substrates by the Spray Pyrolysis Method

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Abstract ZnO micro prisms in thin film form were produced by the low cost spray pyrolysis technique at a substrate temperature of 350 ± 5 °C on glass substrates. Scanning electron microscopy (SEM) and energy dispersion X-ray spectroscopy (EDS) were used to explore morphology and composition of the films respectively. The films were found to be oxygen rich and contain chlorine. ImageJ software was used to analyze the size of the prisms, where the diameter and length of the micro prisms were estimated.

Keywords II-VI compound semiconductors · Transparent conducting oxide · ZnO micro prisms · Solar cells · Spray pyrolysis

Introduction

Wurtzite ZnO with space group P63mc or C6v4 is an important II–VI compound semiconductor material with wide direct bandgap of 3.37 eV at room temperature, and large exciton binding energy of 60 meV at room temperature [1–4]. ZnO is a transparent conductive oxide (TCO) that has promising advantages in optoelectronic devices, solar cells and gas sensors. Nowadays, ZnO is one of the most used TCO materials for thin film silicon solar cell development, and it is of potential use in dye sensitized solid-state solar cells, which are currently the most stable and efficient excitonic solar cells for large-scale solar energy conversion [5–7]. In these cells, 1D ZnO nanorods with high carrier mobility can serve as direct conduction pathways for the excitons [8]. In addition, it is the compound of choice to achieve low-cost, reproducible electrode layers on large-scale production lines. Various physical and chemical techniques have been employed to synthesize ZnO nano/micro structures, such as hydrothermal method [3], chemical vapor deposition

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(CVD) [4], metalorganic chemical vapor deposition (MOCVD) [9–11], sputtering [12], molecular beam epitaxy [13], sol–gel [14], and spray pyrolysis (SP) [15] method. However, for low cost, large-scale production, and intentional doping purposes, the SP method is preferred.

A lot of experimental work was conducted to prepare and characterize ZnO prisms. For example, Ekthammathat et al. [3] produced ZnO prisms on Zn foils by a simple hydrothermal method. Kao et al. [16] deposited ZnO hexagonal prisms on indium titanium oxide-coated glass substrates by using the solution phase deposition method. Hamada et al. [17] deposited these prisms using the electrochemical deposition method on a graphite substrate, and Liu et al. [18] grown them from polyvinylpyrrolidoned-assisted electrochemical assembly onto *p*-type Si (111) substrate. In this work ZnO hexagonal micro prisms were produced on glass substrates using the spray pyrolysis method. These micro prisms are of important use in solar cells, gas sensors, and optoelectronics industry.

Experimental Procedure

ZnO thin films were deposited on glass substrates of dimensions of $60 \times 26 \times 1$ mm^3 by the spray pyrolysis technique at a substrate temperature of 350 ± 5 °C. The starting material was zinc chloride ($ZnCl_2$) of purity 99%. The precursor solution was prepared by dissolving 2.5 g of $ZnCl_2$ in 60 ml of distilled water to get a 0.03 M solution. This solution was sprayed vertically and intermittently on the hot glass substrates, and oxygen was used as the carrier gas. After finishing the deposition process, the heater was turned off, and the samples were left on the heater to cool naturally to room temperature. The morphology of the films was examined by a FEI scanning electron microscope (SEM) (Inspect F 50) operating at 5.0 kV. The composition of the samples was analyzed by the same SEM system, which is supported by energy dispersion X-ray spectroscopy (EDS). The thickness of the films was measured using SEM microscope too. ImageJ software was used to analyze the size of the micro prisms, where both the diameter and length were estimated.

Results and Discussion

Figure 1 displays the SEM images of two ZnO thin films of hexagonal prism micro structure. The film in (a) has a thickness of 1.622 μm, while that in (b) has a thickness of 1.277 μm. The films show high density of ZnO micro prisms where the density in Fig. 1a appears larger than that in Fig. 1b. The difference in density may be due to the larger thickness of the film in Fig. 1a. In this film, three or four positions appear with collections of high density of micro prisms of approximate sizes. In both films, ZnO prisms have hexagonal cross-section, and they appear approximately perpendicular to the surface of the substrate.

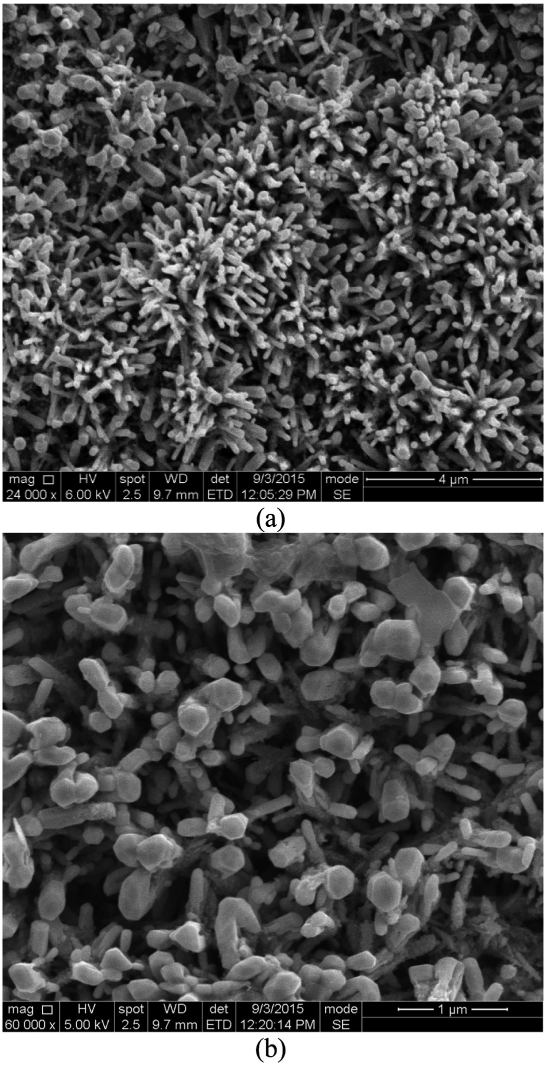
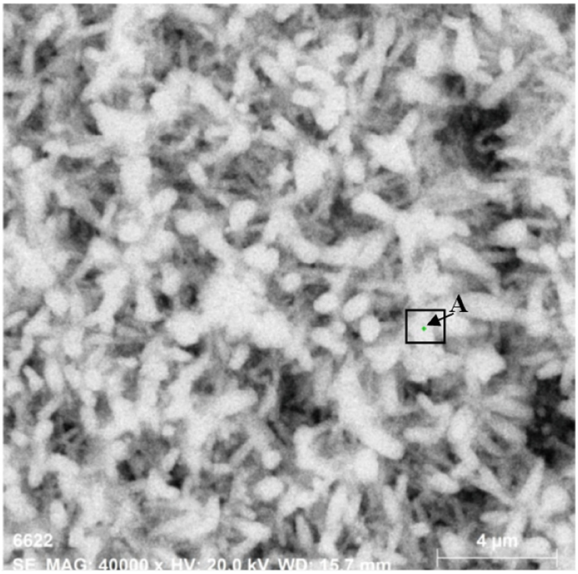
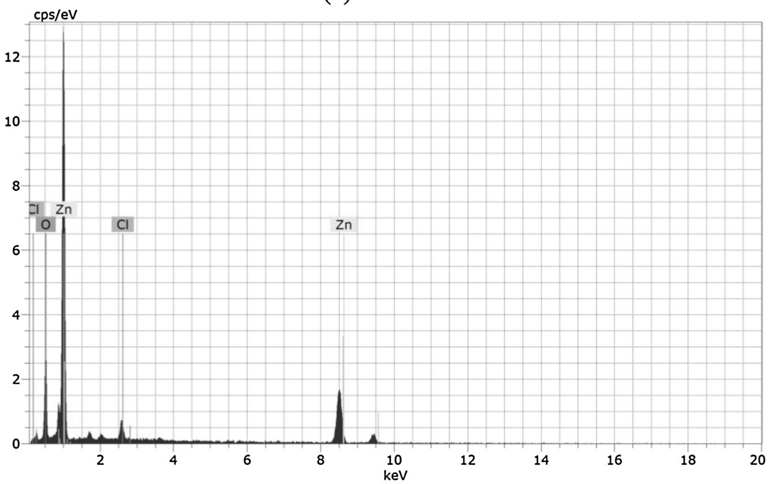


Fig. 1 SEM micrographs of two ZnO films of thickness t = 1.622 μm (**a**), and t = 1.277 μm (**b**)

Figure 2 displays the EDS spectrum of the film in Fig. 1b, in addition to an image showing the point at which measurement was performed. From the EDS report it is found that the films contain Zn, O, and Cl, where the presence of chlorine is due to the use of $ZnCl_2$ as a starting material. The ratio of Zn: O in the film is 37.93: 59.58, or 0.637, while the stoichiometric ratio is 1. This means that the films are oxygen rich. This may be due to the use of oxygen as the carrier gas besides the long period (more than one month) of exposure to air. The EDS report also showed that the ratio of Cl: O in the film is 2.49: 59.58 or 4.18%. When Cl is incorporated in the ZnO crystal lattice, it replaces oxygen, and hence it increases the



(a)



(b)

Fig. 2 SEM image shows the point A at which measurement was performed (**a**), and EDS spectrum for the film of SEM shown in Fig. 1b (**b**)

n-type conductivity of the films, which is preferred in the case of the use of ZnO as a fore contact or a window layer in thin film solar cells.

Figure 3 shows the histograms of the diameter of ZnO micro prisms appearing in the SEM micrographs in Fig. 1a and b, and Fig. 4 shows the histograms of the length distribution for the same micrographs in Fig. 1 too. For the film in Fig. 1a,

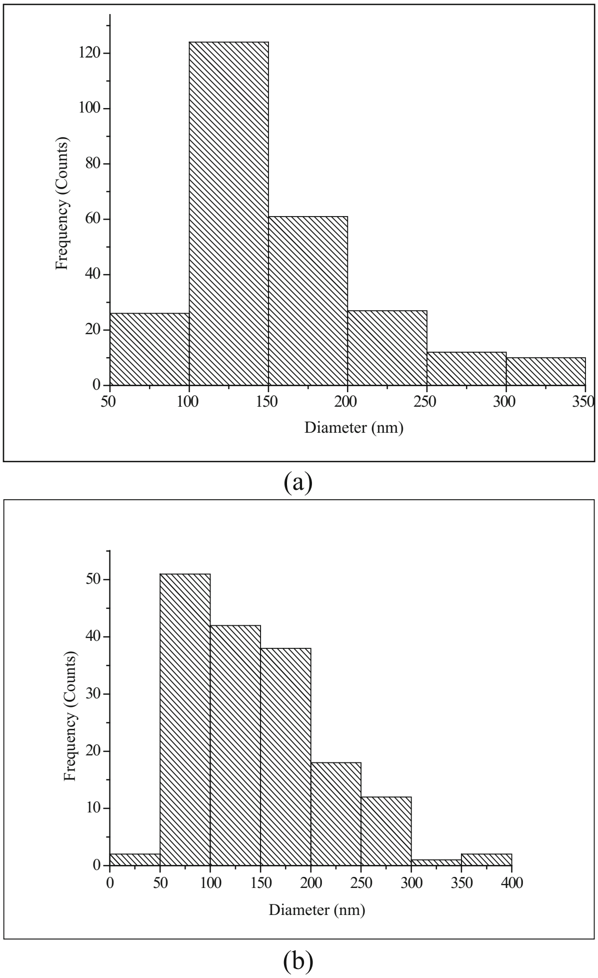
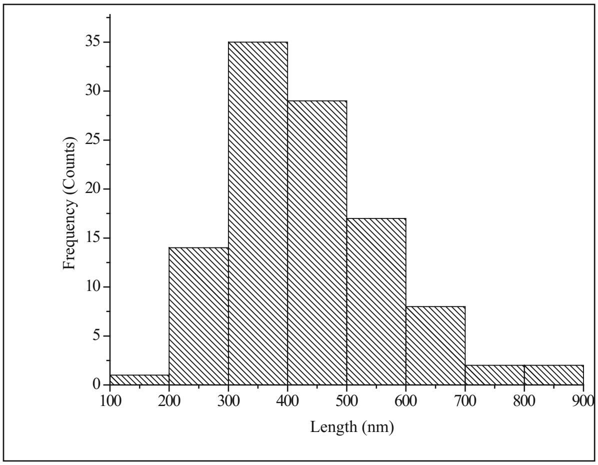
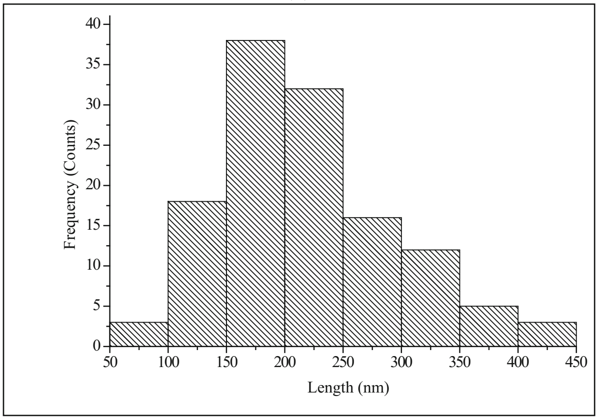


Fig. 3 The histograms of the diameter distributions of ZnO micro prisms in SEM micrographs in: **a** Fig. 1a, and **b** Fig. 1b

the average diameter estimated by imageJ software is $D \pm \Delta D = 156.2 \pm 57.7$ nm, and the average length of the prisms is $L \pm \Delta L = 433.0 \pm 134.6$ nm. Hence the aspect ratio of the prisms in this film is about 2.77. For the film in Fig. 1b, the average diameter is $D \pm \Delta D = 145.3 \pm 68.8$ nm, and the average length is $L \pm \Delta L = 222.1 \pm 74.1$ nm. In this film the ZnO prisms have an aspect ratio of about 1.53. So the prisms in (a) have larger diameter, larger length, and larger aspect ratio. These differences are most probably related to the difference in film thickness in the two cases. The large values of the uncertainties are expected in the case of



(a)



(b)

Fig. 4 The histograms of the length distributions of ZnO micro prisms in SEM micrographs in: **a** Fig. 1a, and **b** Fig. 1b

using the SP method to produce micro and nano structures. There are several factors that determine the size and shape of the produced structures, and to control all of them is a challenge.

Such micro prisms provide larger surface area, which is necessary for several applications such as the dye sensitized solar cells (DSSC). To make a rough estimation of the area of the whole array of micro prisms in the film of Fig. 1a, two assumptions were made. First; no overlap of the micro prisms, and second; the length of the micro prism equals the thickness of the film, where both assumptions are not found in reality. The second assumption may be accepted if there are several layers of the micro prisms are stacked over each other, where the thickness of the film d = NL, and N is the number of layers, while L is the average length of the

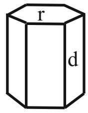


Fig. 5 Prism of hexagonal cross section, radius r and length d = NL

prisms calculated before. Dividing d by L to get N ≈ 4 for the film of Fig. 1a. Hence each four ZnO micro prisms each of length L and diameter D stacked vertically on each will be replaced by one prism of the same diameter and length d as shown in Fig. 5. The area of the portion of such ZnO prism where the dye in DSSC will be adsorbed is $A_{Dye-prism} = \frac{3\sqrt{3}}{2}r^2 + 6rd$, where r is the radius of the hexahedron, and d the thickness of the film in Fig. 1a, which is 1.622 μm. The radius $r = \frac{D}{2} = 78.1$ nm. So $A_{Dye-prism} = 7.6 \times 10^5$ nm^2. If the density of prisms per nm^2 in Fig. 1a is approximated by 10 prisms/nm^2, and the area of the substrate = 60 × 26 mm^2 = 1.56 × 10^{15} nm^2, then the total area of the array ≈ 1.19 × 10^{16} nm^2, which is more than 7 times the area of the substrate.

Conclusions

ZnO Micro prisms were produced as thin films by the low cost spray pyrolysis method on glass substrates. The SEM images showed that the prisms have hexagonal cross sections and they are approximately perpendicular to the substrates. The average diameter, and average length of the micro prisms, besides their distributions were calculated using imageJ software. The EDS reports revealed the composition of the films, and they are found to be oxygen rich and contain chlorine. The estimated surface area of prism arrays on one of the films was found to be seven times that of the substrate. These results are important for the use of such ZnO micro prisms in solar cells and optoelectronic devices.

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