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Structural and spectral properties of ZnO nanorods by wet chemical method for hybrid solar cells applications

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ABSTRACT

The synthesis of ZnO nanorods on transparent conducting oxides, Al doped ZnO seed layer on glass substrate (AZO) and indium tin oxide substrate (ITO) by using zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMT, $(CH_2)_6N_4$ as raw materials is presented. The ZnO seed layer was fabricated by depositing an Al-doped ZnO thin film on glass substrate by sputtering. The effect of seeding on (AZO) and (ITO) substrate by using the wet chemical route growth of ZnO nanorods was investigated. The synthesized nanostructures of ZnO were characterized by X-ray diffraction (XRD), UV–vis absorption spectroscopy, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The results indicate that all the nanostructures of ZnO are preferentially grown as nanorods along [0002] direction (c-axis) of the hexagonal wurtzite structure and the nanorods which are grown on annealed seeded substrate are well shaped hexagonal faceted unlike those formed on non-seeded substrate. However we have observed that when we were increased the aluminum doping on the seed layer the ZnO growth was as nanoplatelets.

1. Introduction

Most of the group II–VI semiconductor materials crystallize in either cubic zinc blende or hexagonal wurtzite (Wz) structure. Among these materials, ZnO is an interesting n-type semiconductor due to its large exciton binding energy (60 meV) and wide band gap (3.37 eV) at room temperature [1–3]. Recently a great variety of ZnO morphologies, such as nanowires and nanorods, have attracted much attention because of their great potential applications in several fields, including electronics [4–6], sensing [7–9], and photovoltaics [10,11]. Various methods are available to grow well-oriented ZnO nanorods. Among them molecular beam epitaxy [12], metal–organic chemical vapor deposition [13], electrochemical deposition [14] and pulsed laser deposition should be emphasized [15]. However, these methods require expensive equipment and complex experimental conditions and they consume a huge energy (high growth temperature). The wet chemical synthesis of ZnO nanorods offers a lot of advantages because it is an environment friendly process and it allows the preparation of ZnO nanorods at much lower temperature and with lower production cost. On the other hand textured transparent conducting oxides are optically transparent and electrically conductive. So they are preferred for optoelectronic applications [16,17]. Vayssieres [18] developed a chemical method to grow arrayed ZnO nanorods on various kinds of substrates by using a zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$). In this work, we have studied the growth of ZnO nanorods on an Al doped ZnO seed layer on glass substrate (AZO) and on the indium tin oxide substrate (ITO).

2. Experimental

The growth of ZnO nanorods was made on transparent conducting oxides, Al doped ZnO seed layer on glass substrate (AZO) and indium tin oxide substrate (ITO) using the wet chemical method. All the reagents, zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) (98%) and hexamethylenetetramine (HMT, $(CH_2)_6N_4$) (99%) were purchased from Sigma-Aldrich and used without further purification. (AZO) and (ITO) substrates ($1 \times 1\ cm^2$) were first

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cleaned with deionized water, ethanol, and acetone and finally dried in a vacuum oven. Next, 1.49 g of zinc nitrate hexahydrate and 0.7 g of hexamethylenetetramine were separately dissolved in 100 ml of deionized water. Then these two aqueous solutions were mixed and magnetically stirred at a ratio of 1:1 for 10 min at room temperature. To grow the ZnO nanorods, the substrates were submerged in this mixed aqueous solution and placed onto a hot plate at a fixed temperature of 90 °C for 5 h. Finally, the samples were removed from the solution, rinsed immediately in deionized water and then dried in air at 50 °C for 10 min. The morphology and the crystalline structure of the ZnO nanorods were measured by SEM, HRTEM, SAED and XRD. The optical properties were also characterized by ultraviolet–visible (UV–vis).

3. Results and discussion

ZnO seed layer: Fig. 1A(a) and (b) shows the XRD pattern recorded for AZO seed layer on glass substrate with and without annealing, respectively. The X-ray diffraction (XRD) measurement was carried out to identify the orientation of the seed layer structures and to characterize crystalline quality. For all the samples the [0002] diffraction peak is dominant, which confirms the preferentially orientated growth along the c-axis to minimize surface free energy and indicates hexagonal wurtzite structure. As can be seen, with annealing of seed layer (a) at 450 °C for 1 h the intensity of (0002) peak also increases.

Table 1 shows full-width at half maximum (FWHM) of (0002) diffraction peak and the grain size of the seed layer with annealing (sample A) and without annealing sample B by using Scherrer's formula

$$D = 0.9\lambda/\beta \cos \theta$$

Here λ, θ and β are the wavelength of Cukα1 radiation, Bragg diffraction angle and full-width at half maximum (FWHM) of the (002) diffraction peak respectively.

The morphology of the seed layer was changed by annealing in nitrogen atmosphere at 450 C° for 1 h as shown in Fig. 2A-1 and A-2. Obviously the surface property of seed layer is improved by annealing and it becomes relatively smoother and more compact.

On the other hand it also demonstrates that the degree of crystallinity of the thin film can be enhanced by annealing. The principal role for the ZnO spectra gives interface trapping levels [19] which effectively interact with the phonon subsystem.

Table 1
Full-width at half maximum (FWHM) of (002) diffraction peak and the grain size of the seed layer without (sample A) and with annealing (sample B) at T=450 °C for 1 h.

Samples	FWHM (deg)	Grain size (nm)	2θ (deg)
Sample A	0.66	12.61	34.79
Sample B	0.46	18.12	35

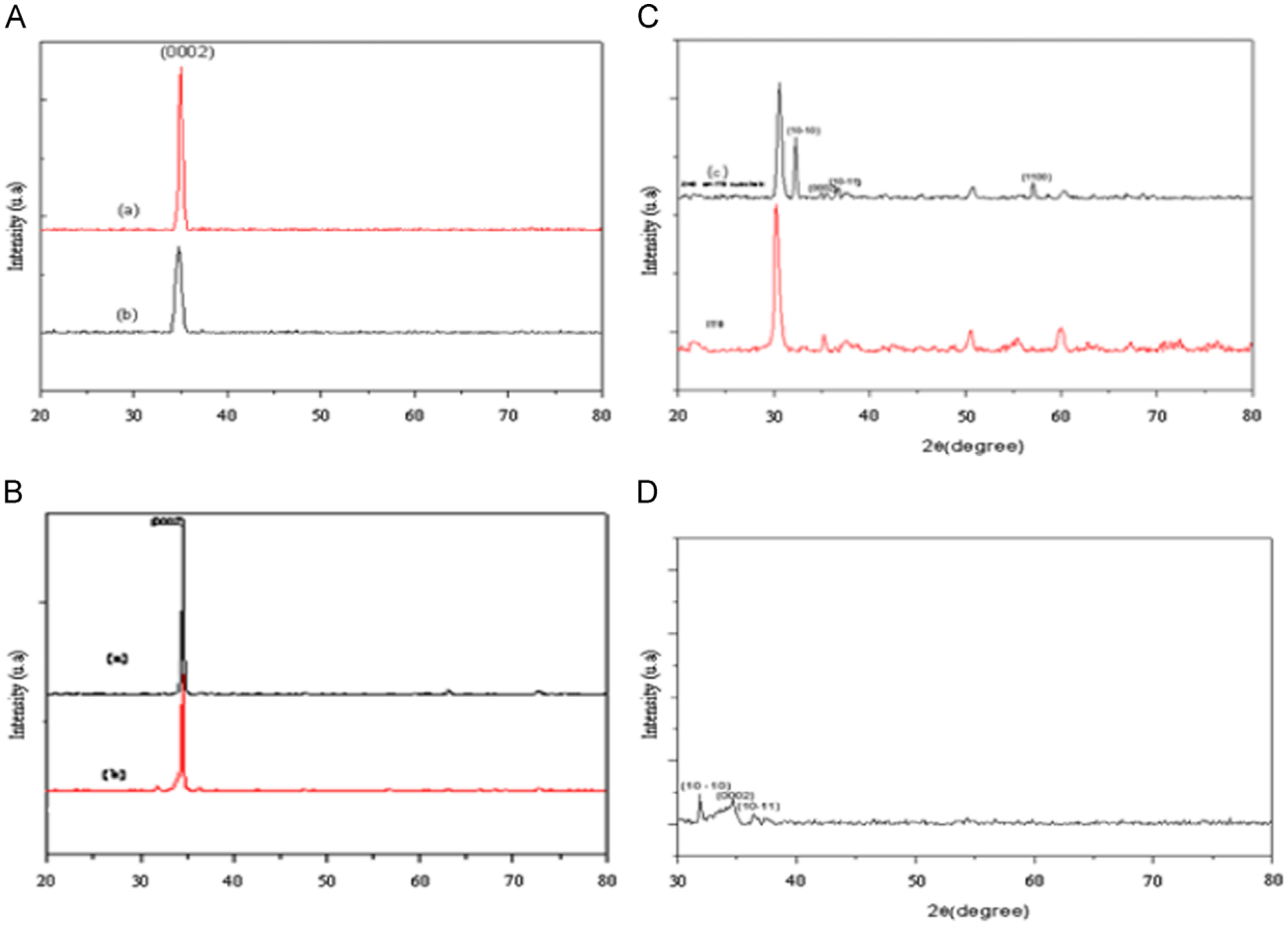

Fig. 1. XRD pattern (A) ZnO seed layer with annealing (a) and without annealing (b). (B) Zinc oxide nanorods on ZnO seed layer (a) with annealing and (b) without annealing. (C) ZnO layer on ITO (c) and without ITO layer (d). (D) ZnO nanoplatelets.