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Growth of ZnO nanowires and their applications for CdS quantum dots sensitized solar cells

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ABSTRACT

ZnO nanowires grown on ITO conductive glass substrates by chemical bath deposition (CBD) method were used as photoanodes to assemble the CdS quantum dots sensitized solar cells (QDSSCs). The growth mechanism of ZnO nanowires and the photovoltaic performance of CdS QDSSCs were investigated. The results show that the *c*-axis oriented seed layer and the growth process both contribute to the preferential alignment of ZnO nanowires along the [0001] direction. The average length and diameter of nanowires increase with increasing growth time, and the maximum aspect ratio is 20.56 at 9 h. CdS quantum dots deposited on ZnO nanowires enhance the absorbance and extend the absorption range to the visible region. ZnO nanowires with higher aspect ratio effectively increase the energy conversion efficiency (η) of CdS QDSSCs, and the best η is 0.401% with an aspect ratio of 20.56. In such a solar cell, the short-circuit current density is significantly improved due to more electron-hole pairs and strong light trapping effect of ZnO nanowires.

1. Introduction

CdS quantum dots sensitized ZnO nanowires solar cells have attracted intense attention recently for the potential applications as photovoltaic devices. One-dimensional (1D) ZnO nanowires possess high electron mobility and surface area, which provide the direct paths for charge transport and efficient light harvesting [1]. CdS quantum dots own a reasonable band gap and high conduction band edge in contrast to the ZnO photoanodes, which are favorable for absorbing visible light and inducing a high open-circuit voltage [2,3]. Thus, high photovoltaic performance of this solar cell can be expected.

Though much effort has been made to the development of ZnO nanowires or nanorods based CdS quantum dots sensitized solar cells (QDSSCs), their energy conversion efficiencies are still relatively low [4–6]. One major challenge is how to prepare well crystallized and aligned 1D ZnO nanostructures. Among various synthesis methods for 1D ZnO nanostructures, chemical bath deposition (CBD) technique has drawn much attention because of its simple coating process, low temperature, reproducibility, and low cost of equipment [7]. In this process, growth parameters such as seed layer, reactant concentration, growth temperature, etc., have been reported to affect the quality of 1D ZnO nanostructures [8–11]. Nevertheless, their growth mechanism should be further understood by exploring the forming process. In this paper, ZnO nanowires were grown on ITO conductive glass substrates by CBD method for different time. The crystallinity and morphology evolutions of ZnO nanowires and the photovoltaic performance of CdS QDSSCs were investigated.

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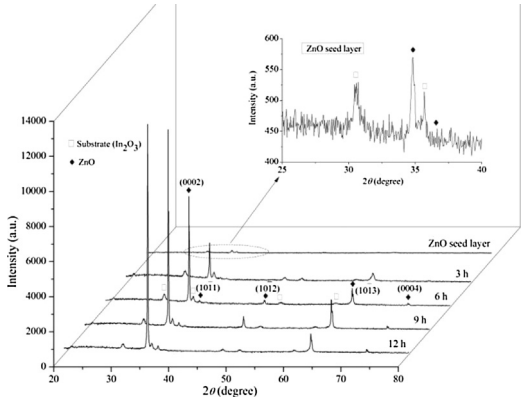

Fig. 1. XRD patterns of ZnO seed layer and ZnO nanowires as a function of growth time. The inset is the enlarged XRD pattern of ZnO seed layer.

2. Experimental

ZnO nanowires were grown on ITO conductive glass substrates by CBD method. Prior to the growth of nanowires, ZnO seed layers (~130 nm) were deposited on the substrates in a pulsed laser deposition (PLD) system which can be evacuated to a base pressure of 10^{-5} Pa. A pulsed KrF excimer laser beam ($\lambda = 248$ nm, $\tau = 10$ ns) with the repetition rate of 5 Hz was focused on the ZnO (99.9% purity) target which was mounted 5 cm apart from the substrate. Depositions were carried out at the substrate temperature of 200 °C, laser energy of 180 mJ/p, and working pressure of 0.8 Pa using O_2 (99.999% purity) as the background gas. Subsequently, the seeded substrates with an area of about 0.7 cm^2 were dipped face-down in an aqueous solution containing 0.05 M zinc nitrate hexahydrate, 0.05 M methenamine and 4.5 mM polyethyleneimine to grow ZnO nanowires. After growth at 95 °C in a water bath for 3–12 h, the samples were thoroughly rinsed with deionized water and dried in air.

CdS quantum dots were deposited on ZnO nanowires by successive ion layer adsorption and reaction (SILAR) method. ZnO nanowires were successively dipped in 0.05 M $CdCl_2$ ethanol solution, ethanol, 0.05 M Na_2S methanol solution and methanol for 30 s, and the dipping procedure was repeated for 12 cycles. For the assembly of QDSSCs, the Pt counter electrodes were prepared by drop-casting an ethanolic $H_2PtCl_6{\cdot}6H_2O$ solution onto the ITO substrates and annealing at 500 °C for 30 min. A seal film under heating (100 °C) was sandwiched between the CdS quantum dots sensitized ZnO nanowires photoanode and the Pt-coated ITO counter electrode. An electrolyte (0.3 M tetra-butyl-ammonium iodide, 0.06 M LiI, 0.03 M I_2, 0.5 M 4-*tert*-butylpyridine in acetonitrile solvent) was then injected into the space between the two electrodes.

The crystallinity and morphology of ZnO nanowires were characterized by X-ray diffraction (XRD, Rigaku D/MAX-RB) and scanning electron microscopy (SEM, FEI Quanta-400). The optical absorption spectra of CdS quantum dots sensitized ZnO nanowires were measured by UV–vis spectrophotometer (PerkinElmer Lambda 950). Current-voltage (*I–V*) characteristics of QDSSCs were recorded by semiconductor device analyzer (Agilent B1500A), and the light source was a 500 W xenon lamp with the illumination intensity of 100 mW cm^{-2}. The incident photon-to-current conversion efficiency (IPCE) was measured by solar cell quantum efficiency measurement system (Zolix, Solar Cell Scan 100).

3. Results and discussion

3.1. Growth of ZnO nanowires

Fig. 1 shows the XRD patterns of ZnO seed layer and ZnO nanowires as a function of growth time. All diffraction peaks are assigned to ITO conductive glass substrate and the randomly oriented hexagonal wurtzite phase of ZnO. But the ZnO (0002) peak is relatively more intense, indicating that the seed layer and nanowires both grow preferentially along the [0001] direction. The result confirms that the vertical growth of ZnO nanowires is strongly related to the (0002) orientation of the seed layer [12,13].

It should be noted that the intensity of ZnO (0002) peak becomes stronger with increasing growth time. In general, the diffraction intensity of (0002) plane depends linearly on the amount of ZnO crystals with *c*-axis aligned paralleling to the substrate normal. As the growth time prolongs, longer nanowires would be obtained to enhance the (0002) peak intensity. Meanwhile, the (0002)/($10\bar{1}1$) peak height ratio increases from 1.27 (seed layer) to 24.2 (12 h), indicating that nanowires becomes more vertical to the substrate. This increase of verticality also contributes to the (0002) peak intensity. Therefore, it can be inferred that the oriented seed layer helps to a certain preferential alignment of nanowires at the initial growth stage, and non-vertical nanowires in the following process would stop growing when encounter the others. This observation differs from the non-preferential orientation of ZnO nanowires without refreshing the growth solution [9].

Cross-sectional and top view images of ZnO nanowires grown for different time are shown in Fig. 2. For each growth period, most of the nanowires are vertically aligned on the substrate, and all nanowires exhibit a regular hexagonal shape,