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Uniform 3D hydrothermally deposited zinc oxide nanorods with high haze ratio

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ABSTRACT

We present low cost hydrothermally deposited uniform zinc oxide (ZnO) nanorods with high haze ratios for the a-Si thin film solar cells. The problem of low transmittance and conductivity of hydrothermally deposited ZnO nanorods was overcome by using RF magnetron sputtered aluminum doped zinc oxide (ZnO:Al ~300 nm) films as a seed layer. The length and diameters of the ZnO nanorods were controlled by varying growth times from 1 to 4 h. The length of the ZnO nanorods was varied from 1 to 1.5 μm, while the diameter was kept larger than 300 nm to obtain various aspect ratios. The uniform ZnO nanorods showed higher transmittance (~89.07%) and haze ratio in the visible wavelength region. We also observed that the large diameters (>300 nm) and average aspect ratio (3–4) of ZnO nanorods favored the light scattering in the longer wavelength region. Therefore, we proposed uniformly deposited ZnO nanorods with high haze ratio for the future low cost and large area amorphous silicon thin film solar cells.

1. Introduction

To overcome the global terawatt energy requirement, amorphous silicon (a-Si) thin film solar cells (TFSCs) have emerged as one of the future candidates for high efficiency, low cost, and large area photovoltaic devices. Light trapping is considered to be one of the essential aspects for the improvement of performance in solar cells, since it can enhance the number of photo-generated charge carriers in the absorber layer and hence reduce the overall size of the solar cell. The reduction of film thickness in a-Si TFSCs is crucial for minimizing the fabrication cost and effect of light induced degradation [1–5]. Various types of light trapping schemes are used to improve the optical and scattering characteristics of front transparent conductive oxides (TCO) films. Commonly used front TCO films for the fabrication of a-Si TFSCs include aluminum doped zinc oxide (ZnO:Al), fluorine doped tin oxide (FTO), boron doped zinc oxide (ZnO:B), and gallium doped zinc oxide (ZnO:Ga), which are deposited by magnetron sputtering, metal oxide-chemical vapor deposition (MO-CVD) or other methods requiring expensive equipment followed by separate wet chemical etching processes [6–8]. However,

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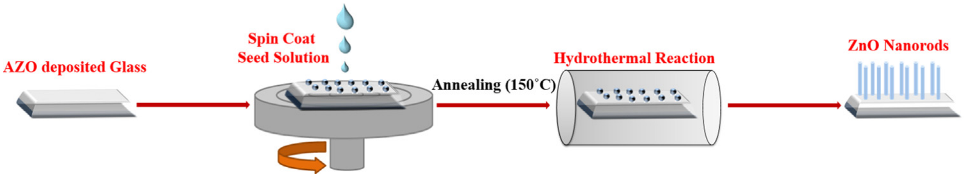

Fig. 1. Schematic diagram for the growth process of ZnO nanorods.

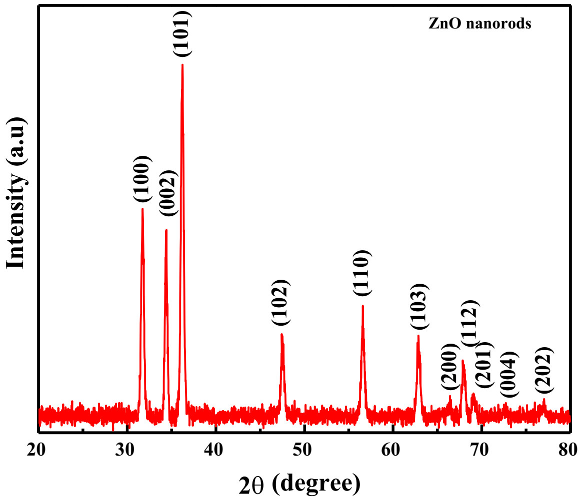

Fig. 2. X-ray diffraction (XRD) patterns of ZnO nanorods.

using these common light trapping methods, only limited size and shapes can be textured. Therefore, a novel low cost light trapping scheme is needed for large area applications. Recently, zinc oxide (ZnO) nanorods, nano-molding, and nano-dome three-dimensional (3D) arrays have been proposed for efficient light scattering in dye sensitized and a-Si thin solar cells [9–11].

ZnO nanorods can be synthesized and deposited using various methods including chemical vapor deposition (CVD), pulsed laser deposition (PLD), chemical bath deposition, aqueous solution, hydrothermal chemical processes, and electro-chemical deposition [9,12–16]. The hydrothermal process is preferred due to its simplicity, large area applications, and low cost deposition. Patil et al. reported vertically aligned ZnO nanorods thin films on steel substrate for CdS quantum dots sensitized solar cell [17]. Kilic et al. reported the fabrication of 3D ZnO nano-flower structures for high quantum and photocurrent efficiency in dye sensitized solar cells [18]. Kuang et al. reported that the ZnO nanorods structure showed better light scattering than randomly textured ZnO films for the applications of 3D nanorods solar cells [19]. Nowak et al. recently proposed low cost electro-chemically deposited ZnO nanorod arrays with high haze ratio as light trapping structures in a-Si TFSCs [9]. Ali et al. reported the novel ZnO/TiO_2-based nano/micro-hybrid heterostructures with high haze ratio for the CdS/CdSe based solar cells [23] that simultaneously offer better light scattering. Various reports have been presented related to hydrothermally deposited ZnO nanorods for dye-sensitized and CdS solar cells, however very few reports are available for the use of ZnO nanorods as a front TCO electrode with high haze ratio for a-Si TFSCs.

In this paper, we show that 3D ZnO nanorod arrays can be used as light trapping structures, additional to their front TCO behavior. We report the influence of ZnO nanorods for high transmittance, haze ratio and low sheet resistance. The surface morphologies and roughness of the ZnO nanorods are discussed for various growth times. The optical transmittance, haze ratio, and sheet resistance of ZnO nanorods are discussed and the XRD and TEM spectra of ZnO nanorods deposited on AZO glass substrates are explained. We briefly explain how these low cost large area ZnO nanorods can be used for the fabrication of a-Si thin film solar cells.

2. Experimental details

ZnO nanorods were grown on AZO based glass substrates via a solution-based hydrothermal method. Prior to the growth, the glass substrates were cleaned by rinsing with acetone, methanol, and deionized water and dried with nitrogen. A uniform AZO (300 nm) layer was deposited on the glass substrates using a RF magnetron sputtering system to improve the transmittance and conductivity of ZnO nanorods. The seed solution was prepared by dissolving 5 mM of $Zn(CH_3COO)_2 \cdot 2H_2O$ and 5 mM of KOH in anhydrous ethanol that was stirred for 10 min. The seed solution was drop cast onto AZO film, placed on a hotplate, and dried at 150 °C for 30 min to achieve good adhesion between the seed layer and AZO surface.

The ZnO nanorods were grown under synthesis conditions, where 0.025 M of hexa-methylene-tetramine (HMTA) and 0.1 M poly-ethylenimine (PEI) were added to 0.025 M of $Zn\ (NO3)_2 \cdot 6H_2O$ aqueous solution and stirred for 30 min. The seeded AZO substrate was then dipped into the precursor solution, followed by the hydrothermal process at 90 °C for a growth time of from 1 to 4 h. The length and diameter of ZnO nanowire arrays can be controlled by altering the growth time, the temperature, and the concentration of the precursor solution. These grown ZnO nanorod arrays were then thoroughly rinsed with DI water and dried with nitrogen gas. Fig. 1 shows the schematic diagram of the ZnO nanorods growth process.

The surface morphology of ZnO nanorods was measured by using a scanning electron microscope (SEM JEOL 7610). X-ray diffraction (XRD) analysis of ZnO nanorods was performed by using the 45 kV, 200 mA (Rigaku Smart Lab XRD, Cu Kα) system. The sheet resistance of the ZnO nanorods was characterized by using a four probe (CMT-series) system. A 3D alpha step profiler (Dektak XT) system was used to measure the rms roughness and 3D surface morphologies of ZnO nanorods deposited on the AZO glass substrates. The optical characteristics (total and diffused transmittance) were measured by using the solar cell