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Low temperature synthesis of ZnO nanowires on GAZO thin films annealed at different temperatures for solar cell application

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ABSTRACT

ZnO nanowires were hydrothermally grown on sputtered gallium and aluminium co-doped ZnO (GAZO) thin films as seed layers and the effect of seed layer annealing temperature on their microstructural and optoelectronic properties was investigated. Atomic force microscopy revealed an increase in the GAZO films' mean particle size and surface roughness with annealing temperature. The GAZO films exhibited a zincite phase with a preferred orientation along the (002) plane and their crystallinity improved with annealing temperature, resulting in low electrical resistivity. The nanowires' alignment improved with seed layer annealing temperature up to 150 °C and then deteriorated at 250 − 350 °C. This was attributed to the improvement in nanowire crystallinity up to 150 °C and its deterioration at 250–350 °C. Energy dispersive spectroscopy confirmed that the nanowires were closer to stoichiometric ZnO (1:1). Raman spectroscopy revealed the presence of few defects and slight residual tensile stress in the nanowires, in corroboration with XRD analysis. The films and nanowires exhibited average visible transmittances around 75–85% and 50–80%, respectively. The least electrical resistivity (7.0×10^{-3} Ω cm) and highest figure of merit (1.02×10^{-2} Ω^{-1}) were obtained for the well-aligned nanowires grown on 150 °C annealed films, demonstrating their suitability for solar cell transparent electrode fabrication.

1. Introduction

ZnO nanowires have attracted significant research attention in the field of short wavelength optoelectronics due to their unique structural one-dimensionality and possible quantum confinement effects in two dimensions [1]. They possess novel properties which make them suitable for use as transparent electrodes in nanogenerators, solar cells, photodetectors, chemical sensors and light emitting diodes [2–4]. ZnO nanowires exhibit a single crystalline structure with few grain boundaries and defects as compared to their bulk and thin film counterparts, leading to their good optoelectronic properties [5]. In addition, ZnO nanowires are more appealing to the bulk or thin film ZnO materials due to their large surface-to-volume ratios [4,6] and efficient charge transport along the wire axis [7].

It is crucial to obtain good device performance through the synthesis of well-aligned ZnO nanowires with better microstructural and optoelectronic properties [8]. During the past few years, several techniques have been developed for the synthesis of ZnO nanowires, including pulsed laser deposition [9], physical vapor deposition [10], chemical vapor deposition [11] and hydrothermal synthesis [8,12]. Among these, the hydrothermal method is cheap, simple, operates at low temperature and atmospheric pressure and is capable of large scale synthesis on any type of substrate [12,13]. However, it is challenging to grow well aligned ZnO nanowires, hydrothermally, on bare substrates because of the large difference in the thermal expansion coefficients and the lattice mismatch which causes larger stress between the nanowires and the bare substrates [10]. Therefore, the hydrothermal method usually employs a seed layer of ZnO thin film to reduce the lattice mismatch between the nanowires and the substrate, thereby effectively improving the length and alignment of the nanowires [14]. The seed layer also supplies the ZnO nucleation centres which act as seed spots where Zn nutrients are consumed during the growth process to produce ZnO nanowires [8,15]. ZnO seed layers have been prepared using numerous techniques such as thermal evaporation [10], sputtering [12,16,17], dip coating [7], spin coating [6,14] and spray pyrolysis [18–20]. However, sputter deposited seed layers are superior to the wet coated ones due to their easy thickness control, strong adhesion of the films to the substrate, good morphology and process repeatability [7,21,22].

The physical properties of ZnO nanowires have been effectively modified through the incorporation of dopants such as Al [2,23–25] and Ga [3,25,26] in their ZnO seed layers. However, tailoring the

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physical properties of ZnO nanowire arrays via the hydrothermal route is still a challenging task. Many researchers have attempted to address this issue by tuning the hydrothermal growth parameters such as growth time, growth temperature and solution concentration. Growth time and temperature were reported to have significant effects on the length [4,5,27,28] while solution concentration had pronounced effects on the diameter of the ZnO nanowires [27–29].

In addition, the underlying seed layer is also vital for the growth of well-aligned ZnO nanowires but until now there is very little understanding on how it affects the growth process [25,30]. Song and Lim [25] and Ji et al. [31] investigated the effect of varying the seed layer thickness on the growth of ZnO nanowires/nanorods and observed an increase in the average diameter and a decrease in the density of the nanowires with increasing seed layer thickness. Seed layer annealing temperature has also been reported to be another critical factor which greatly affects the physical properties of ZnO nanowires [8,14,15,21]. To the best of our knowledge, only a few detailed studies have reported on ZnO nanowires grown by the hydrothermal method on rf magnetron sputtered ZnO seed layers annealed at various temperatures. In the present study, we reveal an optimum seed layer annealing temperature required for the growth of well aligned, transparent and conducting ZnO nanowires by the hydrothermal method on GAZO thin films for the fabrication of solar cell transparent electrodes.

2. Experimental details

ZnO nanowires were grown using the hydrothermal method on glass substrates seeded with rf magnetron sputtered GAZO thin films annealed at various temperatures. Before the synthesis process, the glass substrates were cleaned using acetone, isopropanol and finally deionized water for 15 min in each step with the help of an ultrasonic bath and dried using compressed air. For sputtering, high purity argon was used as the working gas and details of the GAZO thin film deposition conditions are summarized in Table 1.

After deposition, the GAZO thin films were annealed in ambient air for 1 h at 150 °C, 250 °C and 350 °C, respectively. Finally, they were suspended upside-down in a mixture of equimolar 25 mM zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_20$, 99%, Sigma-Aldrich, USA) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, Sigma-Aldrich, 99%, USA) aqueous solutions at 90 °C for 3 h. The chemical reactions that take place during the growth process have been reported elsewhere [32,33]. After the growth process, the samples were removed from the solution and rinsed thoroughly with deionized water and dried in air at room temperature.

Film thickness was measured by a 2D surface profilometer (Alphastep D-100, KLA-Tencor, USA). The surface morphology of the seed layers and nanowires were respectively examined by a Bruker Dimension Edge atomic force microscope (AFM) and a JEOL JSM-7100F field-emission scanning electron microscope (FE-SEM). Elemental compositions were analysed by energy dispersive spectroscopy (EDS) attached to the FE-SEM. The structural properties were characterized by an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) using Cu Kα radiation ($\lambda = 1.5418$ Å) in the 2θ scan range from 10° up to 70°. Raman spectra were obtained in the 70–700 cm^{-1} range, using a Horiba–Jobin Yvon Raman Spectrometer (LabRAM HR Evolution, France) in the backscattering geometry with the 532 nm excitation line of a solid state laser at an incident power of 2 mW. Optical transmittance measurements were done in the 300–800 nm wavelength range, using a UV/Vis/NIR spectrophotometer (Lambda-750, Perkin-Elmer, USA). The electrical resistivity was determined using the Keithley Four–Point Probe equipment.

Table 1
Deposition conditions for the GAZO thin films.

Deposition parameter	Sputtering condition
Substrate	Glass (Corning NY 14831)
Substrate temperature (°C)	100
Target composition (wt%)	Ga/Al/ZnO (1.14/0.62/98.24)
Target-substrate distance (mm)	130
RF power (W)	250
Argon flow rate (sccm)	12
Base pressure (Pa)	1.67×10^{-6}
Working pressure (Pa)	1.78×10^{-3}
Film thickness (nm)	445

3. Results and discussion

3.1. Microstructural properties of GAZO thin films

Fig. 1 shows the three dimensional AFM images of the as-prepared and annealed GAZO thin films, obtained in the peak force tapping mode over a scan area of 1 μm × 1 μm. No cracks were observed on all samples and they showed good uniformity with a flat surface. The root mean square (rms) surface roughness decreased dramatically from 23.9 nm for the as-prepared films to 4.7 nm for the 150 °C annealed films and then increased to 6.2 nm and 6.3 nm for the 250 °C and 350 °C annealed films, respectively, as shown in Table 2. This was comparable with Daniel et al. [34] and Fang et al. [35] who attributed the initial reduction in rms surface roughness to island coalescence and its increase to further grain growth [35]. The increase in mean particle size and rms surface roughness with annealing temperature observed in the present work has also been reported in previous studies [8,14,36,37]. Increasing the annealing temperature causes the GAZO film molecules to have more kinetic energy and this higher molecular motion with excess thermal energy leads to coalescence of the molecules, giving rise to larger particle sizes and higher rms surface roughness [8,36]. Sengupta et al. [36] and Rao and Kumar [37] reported that higher annealing temperature causes atoms to gain enough activation energy such that they occupy the energetically favourable site in the ZnO crystal lattice and subsequently grains with less surface energy grow bigger.

Fig. 2 shows XRD patterns of the as-prepared and annealed GAZO thin films. All diffraction peaks were indexed to ZnO with a hexagonal wurtzite crystal structure (Crystallography Open Database, COD 10 11 258) and all samples had a predominant orientation along the (002) plane, perpendicular to the substrate. The (002) diffraction peak intensity increased significantly with annealing temperature, indicating an improvement in crystallinity. This was comparable with previous studies [36–38]. Annealing causes the atoms to acquire sufficient activation energy to migrate to relatively stable sites in the crystal lattice, with lower surface energy [37]. This subsequently, leads to the development of the growth orientation in one crystallographic direction, the (002) orientation in this case, since it has the minimum surface energy for ZnO, giving rise to the observed increase in (002) peak intensity. This can also be attributed to the increase in self-texturing by annealing which causes most of the grains to have a (002) predominant orientation [37]. No diffraction peaks for any secondary phases were detected on the XRD spectra, indicating that Ga and Al substituted for the Zn sites in the ZnO lattice.

The full width at half maximum (FWHM) decreased from 0.897° to 0.497° while the mean crystallite size increased from 9.28 nm to 16.72 nm with seed layer annealing temperature, suggesting an improvement in crystallinity. Higher annealing temperature caused smaller crystallites to agglomerate by grain boundary diffusion, thereby forming larger crystallites [36,37]. This was consistent with AFM analysis which showed an increase in the mean particle size with seed layer annealing temperature. However, the mean crystallite sizes were smaller than the mean particle size obtained from AFM data, mainly because XRD measures the size of each crystallite while AFM measures the particle size on the sample surface only, of which a particle may contain several crystallites aligned in the same direction [39,40]. Also,