Hydrothermal synthesis of ZnO nanowires on rf sputtered Ga and Al co-doped ZnO thin films for solar cell application

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ABSTRACT

We report the hydrothermal synthesis of ZnO nanowires on rf sputtered gallium and aluminium co-doped ZnO (GAZO) thin films as seed layers. Their morphological, structural, optical and electrical properties were systematically tuned by optimizing the growth temperature, time and solution concentration for application as transparent electrodes in solar cells. The GAZO seed layer had a mean particle size of 77.82 nm, root mean square surface roughness of 6.07 nm and predominant (002) grain orientation. Energy dispersive spectroscopy confirmed the presence of only Zn and O in the ZnO nanowires. Growth temperature and time had pronounced effects on the nanowires' axial growth rate while solution concentration affected their lateral growth. The nanowires adopted a (002) preferred growth orientation of the GAZO seed layer and their crystallinity improved with growth temperature, time and solution concentration. Average optical transmittances around 50—80% were observed in the visible region. Raman spectroscopy confirmed the presence of few defects and negligible residual stress in the nanowires. Well-aligned, hexagonal column shaped nanowires with low electrical resistivity $(1.4 \times 10^{-2} \ \Omega\text{cm})$ and high figure of merit $(8.3 \times 10^{-3} \ \Omega^{-1})$ were obtained with optimized growth parameters (2 h, 90 °C and 25 mM), demonstrating their suitability for transparent electrode fabrication.

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1. Introduction

Transparent conducting oxide (TCO) materials have been of intense research focus in recent years due to their unique properties which enable their application as transparent electrodes in optoelectronic devices such as solar cells, photodetectors, chemical sensors, light emitting diodes and nanogenerators [1—7]. Tin doped indium oxide (ITO) is the most commonly used TCO, due to its excellent optical and electrical properties [8,9]. However, there has been much emphasis on finding suitable alternatives due to the scarcity, high cost and toxicity of indium [10]. ZnO is a promising candidate due to its competitive optical and electrical properties [11,12], together with the abundance in nature, low cost and non-toxicity of Zn [13].

Transparent electrode applications are dominated by surface reaction processes in which ZnO nanowires are superior to bulk or thin film ZnO materials due to their large surface-to-volume ratios [7,14] and efficient charge transport along the wire axis [15]. The large surface area per unit volume also enables ZnO nanowires to enhance the light harvesting properties of solar cell structures [16,17]. Akgun et al. [18] reported that ZnO nanowires exhibit a single crystalline structure with less grain boundaries and defects as compared to their bulk and thin film counterparts, giving rise to their better optoelectronic properties. In addition, the optical and electrical properties of ZnO can be dramatically improved by doping with group III elements such as gallium (Ga) and aluminium (Al), in which the Zn^{2+} ions in the ZnO lattice will be substituted by the higher valent Ga^{3+} and Al^{3+} ions [19—22].

ZnO nanowires are commonly grown using gas phase and solution phase techniques [23,24]. Gas phase approaches can produce highly crystalline ZnO nanowires with high aspect ratios but they require high temperatures, expensive vacuum equipment and often face limitations of sample uniformity, substrate choice and low product yield [25,26]. Among the solution routes, hydrothermal synthesis has been widely used due to its simplicity, low cost, low temperature, no vacuum requirement and large scale synthesis on any type of substrate [23,26].

Prior to the growth of ZnO nanowires, the hydrothermal method usually requires the preparation of a seed layer of ZnO thin film using several techniques such as dip coating [15], spin coating [16],

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spray pyrolysis [27] and sputtering [15,27]. Sathiaraj [9] reported that sputtering is more appealing because of its good reproducibility, high deposition rate and strong adhesion of films to the substrate. Greene et al. [28] also reported that wet coating methods are less reliable and difficult to reproduce since they require several coating cycles and annealing. Bahramian et al. [15] observed no substantial growth of nanowires on un-seeded substrates and reported on the superiority of sputtered seed layers relative to the dip coated ones. The seed layer contains small grains which act as nucleation sites and reduces the lattice mismatch between the nanowires and the substrate thereby effectively improving the length and alignment of the nanowires [29].

ZnO nanowires have been extensively studied due to their easy nanomaterials formation and device application [30]. Optimization of the hydrothermal growth parameters has recently demonstrated the suitability of ZnO nanowires in transparent electrode fabrication through tuning of their electrical resistivity to lower values while maintaining higher transparencies [31]. Jamali−Sheini [32], reported that it is vital to investigate the effect of growth parameters on the morphology of ZnO nanostructures for practical applications since the precise control of the ZnO crystal evolution via a solution route is a formidable task. Also, hydrothermal synthesis is a chemical process, so the solution concentration, reaction temperature and time are vital parameters which affect the reaction rate and subsequently the morphology and optoelectronic properties of the ZnO nanowires [18,33−35]. However, most of the previous studies such as [36−39] have concentrated on optimizing only one of the hydrothermal growth parameters rather than investigating several growth parameters.

To the best of our knowledge, no detailed studies have reported on the electrical properties of ZnO nanowires as well as the optimization of hydrothermal growth parameters of ZnO nanowires grown on GAZO seed layers. Previous works [3,40,41] and [4,39,41,42] have respectively grown ZnO nanowires or nanorods on Ga-doped ZnO (GZO) and Al-doped ZnO (AZO) thin films and reported on their superiority to those grown on undoped ZnO thin films. Muchuweni et al. [21,22] have also reported on the superiority of GAZO thin films to the undoped ZnO, GZO and AZO thin films, suggesting that GAZO thin films as seed layers can lead to the growth of high quality ZnO nanowires. In this work, we therefore present a simple approach of tailoring the ZnO nanowires grown on GAZO thin films to the desired morphological, structural, optical and electrical properties by varying the hydrothermal growth parameters for solar cell application.

2. Experimental

ZnO nanowires were grown hydrothermally on glass substrates seeded with radio frequency (rf) magnetron sputtered GAZO thin films. Prior to seed layer deposition, the glass substrates were cleaned by sonication in acetone, isopropanol and finally deionized water for 15 min in each step and dried using compressed air. The GAZO seed layer was then prepared by rf magnetron sputtering using a 99.99% purity Ga/Al/ZnO (1.14/0.62/98.24 wt%) target (HHV, UK) of diameter, 76.2 mm and thickness, 3 mm. The sputtering conditions included, target to substrate distance of 130 mm, substrate temperature of 100 °C, base pressure of 1.13×10^{-5} mbar, working pressure of 1.20×10^{-2} mbar, rf power of 150 W, argon flow rate of 12 sccm and seed layer thickness of 385 nm. The ZnO nanowires were subsequently grown by suspending the GAZO seeded substrate upside-down in a mixture of equimolar zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$0, 99% purity, Sigma-Aldrich, USA) and hexamethylenetetramine (HMTA, C$_6$H$_{12}$N$_4$, Sigma-Aldrich, 99% purity, USA) aqueous solutions. To investigate the effect of varying the growth parameters, growth temperatures (60 − 90 °C), growth

times (2−8 h) and solution concentrations (5−30 mM) were used, respectively. After the growth process, the samples were removed from the solution and rinsed thoroughly with deionized water to eliminate any residual zinc salts and dried at room temperature in air prior to analysis.

Film thickness was measured by a 2D surface profilometer (Alpha-step D-100, KLA-Tencor, USA) with a sub-angstrom resolution and 0.1% step height repeatability. Surface morphology of the GAZO thin films and ZnO nanowires was characterized by atomic force microscopy (AFM) using a Bruker Dimension Edge AFM in the peak force tapping mode over a scan area of 1 μm^2 and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7100F, Japan), respectively. Elemental compositions were studied by Energy dispersive spectroscopy (EDS) equipped in the FE-SEM. Crystal structure and orientation were examined by an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) operating at 40 kV and 40 mA, using Cu Kα radiation ($\lambda = 1.5418$ Å) in the 2θ scan range from 10 ° to 70 °. The optical transmittance was measured using a UV/Vis/NIR spectrophotometer (Lambda-750, Perkin-Elmer, USA) in the 300−800 nm wavelength range. Electrical resistivity was determined at room temperature from Current-Voltage (I-V) measurements using the Keithley Four−Point Probe equipment. Raman spectroscopy was performed using a Horiba−Jobin Yvon Raman Spectrometer (LabRAM HR Evolution, France) with the 532 nm excitation line of a solid state laser at an incident power of 2 mW in the range 200−800 cm^{-1}.

3. Theory − hydrothermal synthesis

In the hydrothermal synthesis of ZnO nanowires using an equimolar aqueous solution of zinc nitrate hexahydrate and HMTA, zinc nitrate hexahydrate supplies the Zn^{2+} ions required for the formation of ZnO nanowires [40,43]:

$$Zn(NO_3)_2 \cdot 6H_2O \leftrightarrow Zn^{2+} + 2NO^3 + 6H_2O, \tag{1}$$
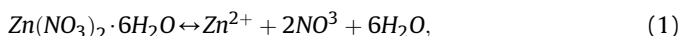
HMTA hydrolyzes slowly in water and gradually forms formaldehyde (CH$_2$O) and ammonia (NH$_3$) [43,44]:

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 6CH_2O + 4NH_3, \tag{2}$$
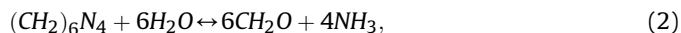
Ammonia then reacts with water to produce hydroxyl (OH$^-$) ions that play a vital role in ZnO nanowire growth [43−45]:

$$NH_3 + H_2O \leftrightarrow NH_4 + OH^-, \tag{3}$$

Therefore, HMTA acts as a pH buffer through the slow production of OH$^-$ ions. Xu et al. [43] reported that if HMTA supplies a large amount of OH$^-$ ions at a faster rate, then the Zn^{2+} ions would quickly precipitate due to high pH, resulting in fast consumption of the nutrient, hence prohibiting the oriented growth of ZnO nanowires. When supersaturated, the OH$^-$ ions combine with Zn^{2+} ions, resulting in the formation of intermediate products such as zinc hydroxide, Zn(OH)$_2$ which can be easily dehydrated so as to form ZnO nanowires through the precipitation of ZnO onto the surface of the seed layer [37,43−45]:

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2, \tag{4}$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O, \tag{5}$$

Reactions (1) to (5) are in equilibrium and can be tuned by adjusting parameters such as growth temperature, growth time and solution concentration to push the reaction equilibrium forward or backward [43−45]. Generally, the growth temperature and time have pronounced effects on the length and aspect ratio of the