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Effect of annealing on the microstructural, optical and electrical properties of ZnO nanowires by hydrothermal synthesis for transparent electrode fabrication

E. Muchuweni*, T.S. Sathiaraj, H. Nyakotyo

Department of Physics and Astronomy, Botswana International University of Science and Technology (BIUST), P. Bag 16, Palapye, Botswana

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ABSTRACT

ZnO nanowires were grown by hydrothermal synthesis and the effect of annealing on their physical properties was investigated by field-emission scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, Raman spectroscopy, spectrophotometry and Hall effect measurements. The nanowires adopted the c-axis [0 0 1] growth orientation of the underlying gallium and aluminium co-doped ZnO seed layer and their vertical alignment improved with annealing temperature up to 250 °C, above which it became random at 350 °C. This was attributed to the improvement in crystallinity up to 250 °C and its deterioration at 350 °C. Energy dispersive spectroscopy confirmed that the Zn:O atomic ratios for all samples were nearly stoichiometric. Average optical transmittances around 50–70% were observed in the visible region. The optimum electrical properties for transparent electrode fabrication were achieved at 250 °C, where the carrier concentration was maximum (5.5×10^{20} cm^{-3}) and electrical resistivity was minimum (1.1×10^{-2} Ω cm).

1. Introduction

ZnO nanowires have gained significant research interest in the past few years due to their novel properties which make them suitable for application, especially as transparent electrodes in optoelectronic devices such as touch screens, flat panel displays, photovoltaic cells, light emitting diodes, nanogenerators and gas sensors [1–4]. ZnO nanowires possess better optoelectronic properties than their bulk and thin film counterparts, due to the nanowires' large surface-to-volume ratios [2,5], efficient charge transport along the wire axis [6] and single crystalline structure which has very few grain boundaries and defects [7].

Numerous techniques such as spray pyrolysis [8], electrochemical deposition [9], chemical vapor deposition [10], physical vapor deposition [11] and hydrothermal synthesis [3,4] have been developed for the synthesis of ZnO nanowires. Among these, hydrothermal synthesis is more appealing due to its low cost, low growth temperature, simplicity, substrate flexibility and large scale production [12]. However, hydrothermal synthesis usually produces ZnO nanowires with relatively poor crystallinity and high defect density [12–14]. Structural defects such as oxygen vacancies, oxygen interstitials, zinc vacancies and zinc interstitials produce potential wells which can trap and reduce carrier movement, thereby degrading the device performance [15,16]. In our previous studies [3,4], we respectively, investigated the effect of hydrothermal growth parameters and seed layer annealing temperature on ZnO nanowires grown on gallium (Ga) and aluminium (Al) co-doped ZnO (GAZO) seed layers. However, some residue was observed on the samples after synthesis and the physical properties of the nanowires required further optimization. Therefore, the thermal treatment of ZnO nanowires after hydrothermal synthesis is vital for the reduction of structural defects, removal of organic ligands obtained from the growth solution and improvement of crystallinity [13,15,16].

Hydrothermal synthesis usually requires a seed layer of ZnO thin film to supply the ZnO nucleation centres [17] and to reduce the lattice mismatch between the ZnO nanowires and the glass substrate, thereby improving the length and alignment of the nanowires [18]. Several deposition techniques such as spray pyrolysis [19–21], spin coating [5,18], dip coating [6,22], thermal evaporation [23] and sputtering [24,25] have been used to prepare ZnO seed layers. Among these, sputtering has the merit of high film uniformity, strong adhesion of the films to the substrate, process repeatability and large scale production [26–28]. Furthermore, the physical properties of ZnO seed layers have been effectively modified through the incorporation of dopants such as Al [29,30–32] or Ga [32–34]. However, co-doping of ZnO with Ga and Al has been reported to produce better film properties

* Corresponding author.
E-mail address: muchuweniedigar1@gmail.com (E. Muchuweni).

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[3,4,22,24,25,35–39].

To the best of our knowledge, no detailed studies have reported on the effect of annealing on the electrical, optical and microstructural properties of ZnO nanowires on GAZO seed layers. In the present study, we reveal an optimum post annealing temperature for the growth of residue free, well aligned, transparent and conducting ZnO nanowires for the fabrication of transparent electrodes.

2. Experimental details

ZnO nanowires were hydrothermally grown on glass substrates seeded with sputtered GAZO thin films. Details of the GAZO seed layer deposition process have been described elsewhere [25], in which the sputtering power and temperature of 150 W and 100 °C were used, respectively. The GAZO seed layer was then suspended upside-down in a mixture of equimolar 25 mM zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_20$, 99%, Sigma-Aldrich, USA) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, 99%, Sigma-Aldrich, USA) aqueous solutions at 90 °C for 100 min. After the growth process, nanowire samples were removed from the solution, rinsed thoroughly with deionized water, dried in air at room temperature and annealed in ambient air for 60 min at 150 °C, 250 °C and 350 °C, respectively.

Film thickness was measured by a 2D surface profilometer (Alpha-step D-100, KLA-Tencor, USA). Surface morphology was characterized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7100F, Japan). Elemental compositions were analysed by energy dispersive spectroscopy (EDS) attached to the FE-SEM. Crystal structure and orientation were examined by an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) using Cu Kα radiation (λ = 1.5418 Å) in the 2θ scan range from 10° to 70°. Raman spectroscopy was performed in the 70–700 cm^{-1} range, using a Raman Spectrometer (Horiba–Jobin Yvon, 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 performed using a UV/Vis/NIR spectrophotometer (Lambda-750, Perkin-Elmer, USA) in the 300–800 nm wavelength range. Electrical properties were determined at room temperature using the Hall effect measurement system (HMS-5500, Ecopia, South Korea) in the van der Pauw configuration.

3. Results and discussion

3.1. Microstructural properties of the GAZO seed layer

The seed layer provides grains which act as nucleation centres for the growth of nanowires. The size of these grains has a significant effect on the nanowire morphology and can be determined by SEM analysis. Fig. 1 shows the (a) SEM micrograph and (b) EDS spectrum of the GAZO seed layer prepared by rf magnetron sputtering. From Fig. 1(a), it can be seen that the GAZO seed layer was uniformly covered with almost spherical grains of mean diameter around 80 nm. This was consistent with Dong et al. [40] who reported that the uniform size distribution of sputter deposited seed layers promotes the growth of nanowires with a predominant c-axis orientation and uniform height. From Fig. 1(b), EDS detected the elements Zn, O, Ga and Al, thereby confirming the formation of the GAZO seed layer.

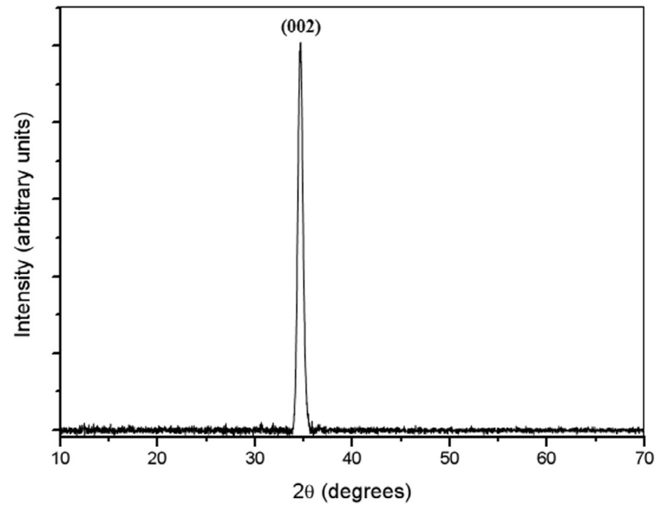

Fig. 2. XRD pattern of the GAZO seed layer.

Fig. 2 shows the XRD pattern of the sputter deposited GAZO seed layer. The GAZO seed layer had a hexagonal wurtzite structure with a predominant (0 0 2) peak intensity, indicating the prevailing presence of crystals with a c-axis [0 0 1] growth orientation, perpendicular to the substrate. The (0 0 2) peak position (34.677°) was slightly higher than (34.467°) for bulk ZnO (Crystallography Open Database, COD 10 11 258) and this was attributed to small amounts of compressive strain (-5.1×10^{-3}) and tensile stress (1.2 GPa) in the GAZO seed layer. The strain and stress probably originated from the substitution of Zn^{2+} ions with relatively smaller Ga^{3+} and Al^{3+} ions and the thermal mismatch between the film and substrate. The mean crystallite size (15.77 nm) obtained from XRD data was smaller than the mean grain size (80 nm) determined by SEM analysis, implying that a grain possibly contained several crystallites.

3.2. Microstructural properties of the ZnO nanowires grown on the GAZO seed layer

Fig. 3 shows FE-SEM micrographs of the as-prepared and annealed ZnO nanowires. All sample surfaces were uniformly covered by ZnO nanowires with hexagonal cross-sections and this was related to the

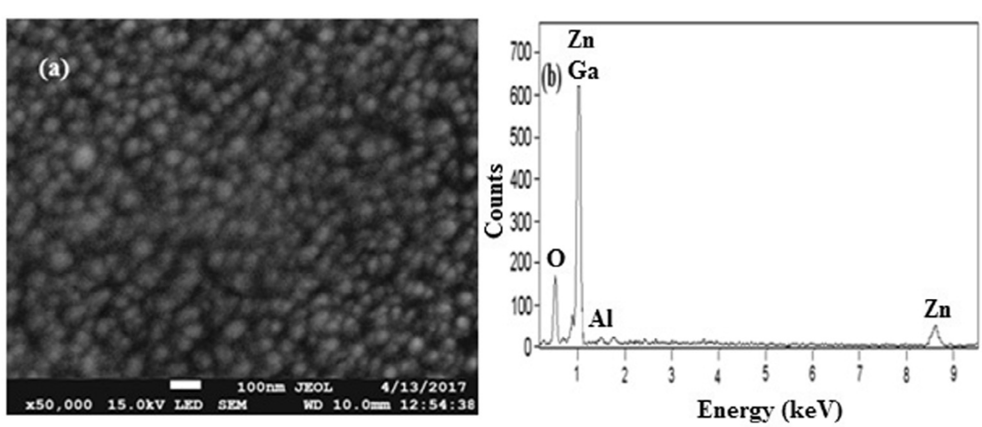

Fig. 1. (a) SEM micrograph and (b) EDS spectrum of the GAZO seed layer prepared by rf magnetron sputtering.