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The growth and conductivity of nanostructured ZnO films grown on Al-doped ZnO precursor layers by pulsed laser deposition

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Abstract

The structure and electrical properties of nanostructured Al-doped ZnO (AZO)/ZnO bilayers grown as potential solar cell electrodes by pulsed laser deposition on (0001) sapphire substrates are investigated. Transmission and scanning electron microscopy and X-ray diffraction show a narrow temperature window around 350–450 °C where nanostructures are formed. 2-D mapping of electrical conductivity by tunnelling atomic force microscopy showed that these nanostructures provided low resistance pathways, but that the overall film resistivity increased for substrate temperatures above 350 °C. The reasons for this are discussed.

Keywords: Al-doped ZnO (AZO) and ZnO thin films; Pulsed laser deposition (PLD); Scanning electron microscopy (SEM); Transmission electron microscopy (TEM); Tunnelling atomic force microscopy (TUNA)

1. Introduction

Zinc oxide is a type II–VI semiconductor, with well-established uses in optoelectronic devices. Intrinsic defect levels mean that it is usually an n-type semiconductor. It has an exciton binding energy of 60 meV at room temperature and high electron mobility with a direct band gap of 3.37 eV. In addition, ZnO can be grown in nanostructured forms, including nanorods, by a range of techniques including sputtering [1], chemical vapour deposition (CVD) [2] and pulsed laser deposition (PLD) [3,4]. This has led to particular interest in the growth of nanostructured ZnO electrodes with high surface area for third generation solar cells [5,6].

Many research groups have reported the effect of growth parameters such as substrate temperature [7–10], laser repetition frequency [11], substrate types [12] and the background oxygen pressure [13] on the growth of nanostructured ZnO thin films by PLD. All these ZnO films were grown on bare substrates such as Si, sapphire, GaAs, and glass. It has been found that the substrate temperature plays a crucial role in the growth of ZnO films by PLD.

Generally, ZnO has been doped with group (III) elements such as Ga, In and Al giving carrier concentration levels up to 10^{20} cm^{-3} [14,15]. However, Al is widely chosen to dope ZnO for transparent conducting oxide (TCO) applications [16,17]. The Al-doped ZnO (2 wt% Al_2O_3) precursor layer provides a conducting substrate, and has been considered widely as a viable, cheaper and more environmentally friendly alternative to indium tin oxide (ITO), which is presently used as a transparent conducting electrode in many flat screen displays and solar cells. A variety of studies has demonstrated that ZnO has a relatively low resistivity when doped with Al (10^{-3}–10^{-5} Ω cm) [3,18,19].

The purpose of this study is to examine the electrical properties of the AZO/ZnO nanorod combination and see whether one can combine good electrical properties of the AZO with acceptable electrical properties of the ZnO nanorods. The structures examined in this paper are illustrated schematically in Fig. 1. Changes in the structure of the films as a function of the substrate temperature are investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Tunnelling atomic force

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microscopy (TUNA) is used to examine the conductivity at the microscopic level on individual nanostructures, and the overall electrical properties of the films are examined using a standard four point probe technique.

2. Experimental methods

ZnO films on Al-doped ZnO (AZO) precursor layer were grown by PLD using a 193 nm Excimer Pulsed UV-ArF laser (Lambda-Physic COMPex 201, pulsed at 10 Hz). The target materials for PLD were 99.999% pure ZnO and a 99.999% pure ZnO (98 wt%):Al_2O_3 (2 wt%) (Cerac). The target was rotated at ~2 rpm in order to prevent ablation of the same area. The growth chamber was evacuated to a typical base pressure of $\sim 1 \times 10^{-6}$ Torr using a turbo molecular pump. The chamber was backfilled with oxygen in order to maintain a constant pressure ~10 mTorr. The substrate, (0001) sapphire, was positioned at a distance of 4 cm from the target on a halogen bulb heater. The substrate was mounted on the glass surface of the halogen bulb using silver conducting paint and subsequently allowed to dry in air for ~30 min. The substrate temperature was measured by using a digital thermocouple contacted to the front surface of the sample using silver conducting paint. Prior to deposition, the substrate surface (1 cm × 1 cm) was initially washed with acetone and then with ethanol. An AZO seeding layer was deposited at 350 °C for 15 min with a pulse energy of 3 J/cm^2. Then the AZO target was replaced by ZnO and ZnO layers were deposited for 45 min at a pulse energy of 3 J/cm^2 for temperatures in the range 350–650 °C.

The structure of the films was analysed by transmission electron microscopy (TEM) on cross-sectional samples using a Philips EM 430 microscope, and by scanning electron microscopy (SEM) of the as-grown samples using a JEOL JSM 6330 F. Tunnelling atomic force microscopy (TUNA) was performed using a Bruker Multimode V controller with a J-scanner and a TUNA 2 module. Imaging was performed using Pt/Ir coated Antimony (n-type) doped silica tips (Bruker SCM-PIC, 0.01–0.025 Ω cm^{-1}, K=0.2 N m^{-1}). Samples for imaging were prepared by affixing the ZnO coated layer to a magnetic stub using silver conductive paint (Agar). Current–voltage curves were taken by imaging the TUNA current and then using the microscope in ramp mode to plot DC sample bias versus detected current. Images were processed using Gwydion open source software. Current–voltage curves were processed using the Nanoscope version 7.2 software.

The crystalline structure of the ZnO films was investigated by X-ray diffraction (BRUKER D8 advance). The output of the X-ray source (Cu-Kα radiation with Ni filter, wavelength 1.5417 Å) was fixed at 40 kV and 40 mA and the scan range for 2θ was measured from 30° to 40°. The room temperature photoluminescence (RT-PL) studies were carried out using a Renishaw CdTe Laser (325 nm). The spectra were acquired by WiRE 2.0 computer interface program. Finally a four point probe technique was used to measure the conductivity of the samples via Labview-7 interface program.

3. Results and discussion

3.1. SEM and TEM analysis

Fig. 2(a–d) shows the SEM images of ZnO film grown at 350 °C, 450 °C, 550 °C and 650 °C, viewed from the normal to the surface. The films grown from 350 °C to 550 °C exhibit wool-like structures. At 550 °C (Fig. 2c), some nanotube-like structures (indicated by arrows) with a diameter of 80 ± 13 nm can be observed. The TEM studies reveal (Fig. 3c) that there are solid nanorods with a diameter of 60 ± 17 nm, which is seen more clearly by tilting the sample ± 50° about the nanorod axis. The tapering of the rods seen in the TEM images may be an artefact generated by the ion polishing preparation technique used to prepare the sample for cross-sectional TEM imaging. The polishing

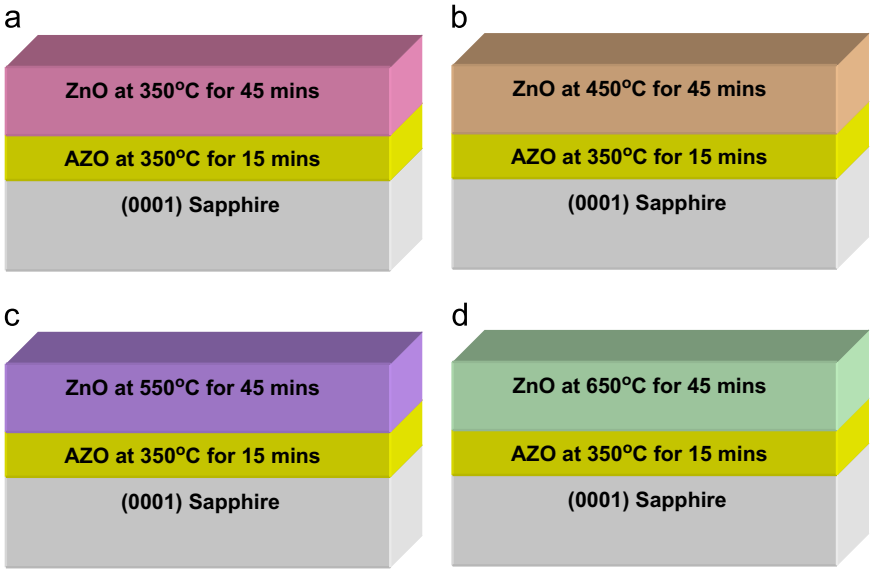

Fig. 1. Schematic diagrams showing the structures of the four different samples (a)–(d) used during this research.