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Structural, surface morphological and UV photodetection properties of pulsed laser deposited Mg-doped ZnO nanorods: Effect of growth time

P.S. Shewale [a], Y.S. Yu [a, b, *]

[a] Convergence of IT Devices Institute, Dong-Eui University, Busan 614-714, South Korea
[b] Department of Radiological Science, Dong-Eui University, Busan 614-714, South Korea

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ABSTRACT

$Mg_{0.05}Zn_{0.95}O$ (MZO) nanorod (NR) array films have been successfully grown on SiO_2/n-Si substrates by pulsed laser deposition (PLD) without any seed layer. The effect of growth time (15–60 min) on the structural, surface morphological and UV sensing properties of the aligned MZO NRs were studied. All the samples exhibit the hexagonal wurtzite phase with a preferential c-axis orientation that improves on increasing growth time. FESEM images demonstrated that the MZO NRs grow with better alignment and greater size for elongated growth durations. The UV photodetection characteristics of MZO NRs were investigated in metal–semiconductor–metal (MSM) planar configurations at room temperature and are found to be greatly dependent on growth time. The photocurrent increases with an increase in the growth time due to improvement in film crystallinity and mean surface area of nanorods. Both the photocurrent and responsivity were further measured with the variation of optical power density and applied voltage, respectively. Exceedingly stable and fast switching UV photoresponse is seen for the photodetector having MZO NRs arrays grown for 60 min, which shows highest responsivity of 22.33 mA/W upon 2 mW/cm^2 UV illumination (365 nm) at 5 V applied bias.

1. Introduction

Recently, the wurtzite magnesium (Mg) doped ZnO or MgZnO thin film materials have received increasing interest due to their excellent optoelectronic properties of the parent structure of ZnO and multiple applications. The MZO thin films observed to possess advantageous features such as tunable wide direct band gap, large exciton binding energy, and low growth temperature [1–3]. The lattice constants of MZO seen to remain virtually unaffected even after Mg incorporation as a result of the high solid solubility of MgO in ZnO [4,5]. Reportedly, the incorporation of Mg into ZnO lattice reduces the interstitial oxygen vacancies and electron density [6]. Therefore, MZO thin film exhibits tunable electrical and optical properties and it has established as a feasible active layer in optoelectronic devices such as ultraviolet (UV) photodetectors (PDs) [7].

As we know, the ZnO nanostructures like nanorods (NRs), nanowires (NWs) etc. have attracted much attention of the research community attributable to their size and shape dependent optical response and relatively easy fabrication. Several physical and chemical methods have been employed to prepare arrays of ZnO NWs and NRs with the help of seed layer/templates, catalysts, and doping etc [8–16]. Particularly, the seed layer has been applied widely to grow NRs that apparently reduces the lattice mismatch between the NRs and a substrate and leads to the growth of well-aligned NRs on the substrate [17,18]. Many efforts have also been reported on growth of ZnO NRs using the simple and versatile pulsed laser deposition (PLD) technique with or without any prior templating [19–23]. Application of high growth temperatures (>550 °C) and/or high oxygen background pressure (>1 Torr) during the PLD process was proven useful for growing ZnO nanorod arrays without any templates. For example, Sun et al. had grown ultrathin needle-like ZnO NRs on Si substrates using catalyst-free PLD at 600 °C and low pressure (~10 mTorr) [21]. Liu et al. synthesized ZnO NRs on sapphire and silicon substrates by a PLD technique using relatively high background oxygen pressure (5–20 Torr) and substrate temperature (550°C-700 °C) and studied their room temperature photoluminescence (PL) properties [22]. Further, Liu at al also investigated the effect of the PLD process on the morphology and characteristic size of the ZnO NRs prepared under a high background pressure and a relatively high

* Corresponding author. Department of Radiological Science, Dong-Eui University, Busan 614-714, South Korea.
E-mail address: ysyu@deu.ac.kr (Y.S. Yu).

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temperature without catalyst [23]. Although such reports on the synthesis of ZnO NRs are available in the literature, the seed layer free growth of well-aligned MgZnO NR films by PLD and their UV photoresponse properties had hardly ever been reported, to the best of our knowledge.

In this paper, we report the synthesis of $Mg_{0.05}Zn_{0.95}O$ (MZO) NR films by PLD technique under a relatively low (<1 Torr) background oxygen pressure and high temperature without any templates. The MZO NRs with different diameters (100–500 nm) were grown-up on insulating SiO_2/n-Si substrates by varying the growth time, and hence their crystallinity, surface morphological features and UV photodetection performance in MSM configurations have been investigated and discussed.

2. Experimental

2.1. Pulsed laser deposition of MZO thin films

To realize 5 at% Mg incorporation in ZnO, firstly, the target was prepared from high purity ZnO powder (99.99%, Aldrich Chemical Company, Inc. USA) doped with MgO (99.99% Kanto Chem. Co., Japan). The disk shaped target (24 mm with a diameter and 5 mm in thickness) was prepared by employing a uniaxial pressing at 700 kg/cm^2, followed by a cold isostatic press at 24,000 kg/cm^2 to the powder. Then, the disk-like target sample was sintered at 700 °C for 4 h and at 1200 °C for 4 h for its further densification. The as-sintered target was then mounted onto the target holder using epoxy resin.

To obtain SiO_2/n-Si substrates, initially, an insulating layer of SiO_2 (~480 nm thick) formed over the n-Si (100) wafer surface by the wet oxidation method. Before being loaded into the wet oxidation chamber, the silicon wafer was rinsed in acetone, ethanol, distilled water, and dried by nitrogen gas. Such SiO_2/n-Si wafer was cut into 1 × 1 cm^2 sized pieces; so that it can be used as substrate in the PLD chamber. The SiO_2/n-Si substrate was attached to the heater with the help of silver paste and the heater in place into the PLD chamber opposite to the target. To ensure uniform ablation without damaging, the target was constantly rotated (at 10 rotations/min) throughout the deposition. A KrF excimer laser (Coherent Inc. COMPEX pro205F, USA, $\lambda = 248$ nm, $\tau = 25$ ns), working at 5 Hz repetition rate and 200 mJ/cm^2 energy density was used to deposit MZO films on SiO_2/n-Si substrates from target with various growth times, i.e. 15, 30, 45, and 60 min. During deposition, the substrate temperature was kept at 700 °C, while the oxygen pressure was maintained constant at 2×10^{-1} Torr. Responding to the reduced plume length due to increasing background pressure, the target to substrate distance was adjusted to 4 cm. The laser beam was focused through 50 cm focal length lens on a continually rotating MZO target at a 45° incidence angle.

2.2. Characterization and UV photodetection studies

The crystallographic studies of as-prepared MZO NR films were carried out using X-ray diffraction (XRD) using X-ray diffractometer [Rigaku, D/MAX 2100H Model] with Cu K_α radiation having wavelength 1.5406 Å. All the diffraction patterns were recorded by varying the diffraction angle in the range of 20–60°. The average film thickness was measured from cross-sectional field emission scanning electron microscopy (FE-SEM) images, and the mean of the number of measurements made at different locations was reported for each sample. The surface and cross-section FE-SEM images were obtained by Quanta 200 FEG & FEI Company FE-SEM equipment. The elemental analysis was done by using an energy dispersive X-ray spectrometer (EDX) attached to FE-SEM.

To test the room temperature photoconductive UV detection performance in metal–semiconductor–metal (MSM) configuration, the ohmic contacts were prepared by using pressed aluminium (Al) foil layers onto the pulsed laser deposited MZO NRs. The forward and reverse current–voltage (I–V) characteristics of these MSM devices were measured by means of Keithley instruments model 2410 Sourcemeter. Before the dark I–V characteristics measurement, the MSM devices were kept under the dark for more than 24 h to stabilize the dark current. A mercury arc lamp was used as the UV light source ($\lambda = 365$ nm) during the UV photocurrent measurements. The photocurrents of all the MZO NRs films based MSM UV photodetectors were measured under UV light exposure of different incident optical powers, by applying a constant bias of 5 V. Lastly, the photocurrent response to UV light was examined by switching the UV light source of 2 mW/cm^2 intensities at different time intervals.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of the MZO films prepared with various growth times. From the figure it is seen that the film growth is along (1 0 0) and (0 0 2) plane. It is further observed that the growth is preferentially oriented along (0 0 2) plane. The comparison of observed and standard 'd' values confirms the formation of MgZnO hexagonal wurtzite structure. No other phases in the samples can be observed. The preferentially c-axis oriented growth of all the films is attributed to a surface-energy-driven self-texturing mechanism [24]. Close inspection of Fig. 1 reveals that there is a slight change in (002) diffraction peak positions; especially for the growth duration longer than 30 min. The angular position of the (002) diffraction peak shifts towards the lower angle (2θ) as growth time increases above 30 min. The observed shift in the (002) diffraction peak position to lower angles implies lattice expansion due to stress, which may have been caused by a combination of (i) intrinsic defects (e.g. zinc interstitial or oxygen vacancies) in the MZO matrix and/or (ii) the strain at the MZO film/substrate interface because of the lattice mismatch [25]. Moreover, crystalline quality of MZO NRs improves on increasing the growth time. Actually, the XRD patterns show that when growth time is increased, the intensity of the XRD peak increases monotonously. Also, the width of the observed (002) peak shows a systematic contraction with increasing growth time. These two co-existing

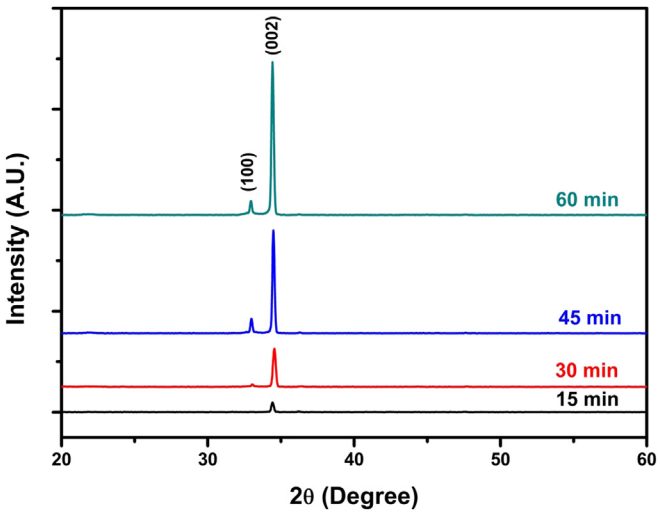

Fig. 1. XRD patterns of MZO films with various growth durations.