

Full Length Article

Hydrothermal growth and luminescent properties of nonpolar *a*-plane (11–20) ZnCdO films for light-emitting diodes

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ABSTRACT

Nonpolar *a*-plane ZnCdO films have been obtained on *a*-plane GaN using a simple low-cost hydrothermal growth method at the low temperature of 80 °C. The morphological, structural, optical, and electrical properties of *a*-plane ZnCdO films with various Cd contents have been investigated and compared. The photoluminescence peak of the *a*-plane Zn_{0.957}Cd_{0.043}O film, was observed to be centered at 429 nm at 25 °C. We demonstrated a heterostructure light-emitting diode (LED) using nonpolar n-type Zn_{0.957}Cd_{0.043}O/p-type GaN films. The rectifying behavior of the current-voltage characteristics was observed with a turn-on voltage of 5 V. The electroluminescence of the LED showed emission peaks including 430 nm, which indicates the near-band-edge emission of *a*-plane Zn_{0.957}Cd_{0.043}O at 25 °C.

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1. Introduction

ZnO-based semiconductors have been the focus of intensive research for applications in light-emitting diodes (LEDs), laser diodes, photodetectors, and sensors [1–7]. As an alternative material for conventional GaN, ZnO has the same hexagonal wurtzite structure and a similar wide bandgap of 3.4 eV as GaN. ZnO has a larger exciton binding energy of 60 meV, as compared to that of GaN (25 meV), and can be easily etched using various wet chemical solutions [3,7,8]. ZnO epitaxial layers have been grown using a variety of techniques including metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy, pulsed laser deposition, sputtering and hydrothermal synthesis [3,4,7,9–11]. Among these deposition techniques, hydrothermal growth is one of the most facile cost-effective methods owing to its low-temperature process at atmospheric pressure [3,4,11]. Most hydrothermally-grown ZnO grow in the shape of a nanorod or nanowire along the *c*-axis [0001] direction since the growth rate in the *c*-plane (0001) is faster than in the other planes [3,11]. It is still challenging to achieve stable and reproducible p-type ZnO for optoelectronic applications owing to its self-compensating effect from oxygen vacancy and hydrogen interstitials with shallow donor energy level, and large activation energy and low solubility of acceptor dopants [8,10,12–14].

As an alternative approach, heterostructure LEDs with n-type ZnO nanorods grown on *c*-plane p-type GaN substrate have been proposed [15–17]. However, the electron-hole recombination region is limited only to the interface between ZnO nanorods and GaN film, and randomly distributed ZnO nanowire features are not compatible with the established semiconductor manufacturing process. Moreover, it is well-known that spatially separated electron and hole wave functions in the quantum well (QW) of the conventional *c*-plane heterostructure by the internal spontaneous and piezoelectric field result in the reduction of internal quantum efficiency (IQE) of the LEDs [3,4]. For example, the built-in electric field in ZnO/ZnMgO QW along the *c*-axis direction was as large as 0.9 MV/cm [18]. In order to eliminate the internal electric field in the LED, nonpolar *a*-plane (11–20) crystal structures, where Zn cations and O anions exist equivalently on the surface and form zero net dipole in the plane, can be used [3,4].

Bandgap engineering is one of most important elements in LEDs. By employing a QW structure consisting of small bandgap InGaN active layers sandwiched between GaN barriers, the IQE of GaN-based LEDs was significantly improved [18,19]. Since CdO has small direct bandgap of 2.3 eV, the bandgap energy of ZnO-based material system is tunable by controlling the amount of incorporated Cd in the ternary ZnCdO alloy while maintaining the crystalline structure of ZnO [2,20–22]. Growth of ZnCdO on *r*-, *m*-, or *a*-plane sapphire substrate by using complex growth systems such as metal-organic vapor phase epitaxy (MOVPE), pulsed laser deposition (PLD), and remote-plasma-enhanced metalorganic chemical vapor deposition

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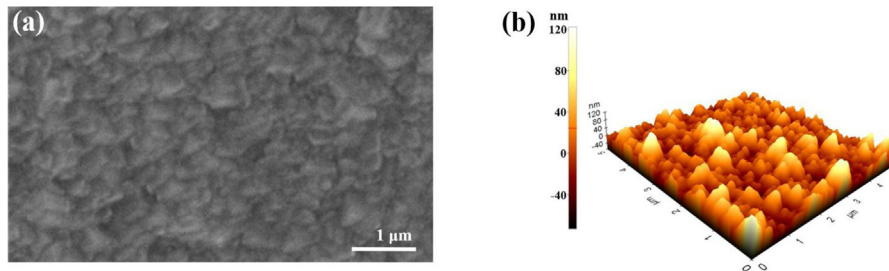


Fig. 1. (a) SEM and (b) AFM images of a -Zn_{0.957}Cd_{0.043}O grown by hydrothermal method on a -GaN.

(RPE-MOCVD) have been reported by other research groups previously [23–26]. In this study, a nonpolar a -plane ZnCdO (a -ZnCdO) epitaxial layer was successfully grown on a -plane GaN (a -GaN) by simple low-cost hydrothermal method at the low temperature of 80 °C. The structural, morphological, and optical properties of a -ZnCdO film with various Cd contents were investigated. Moreover, hydrothermally grown nonpolar n -type a -ZnCdO/ p -type a -GaN heterojunction LED was demonstrated and characterized.

2. Experiment

Planar a -plane (11–20) GaN epitaxial films were grown on r -plane sapphire substrates utilizing a two-step growth method with AIX 2400 G3 MOCVD system. After the thermal cleaning in nitrogen atmosphere, a 150-nm-thick nucleation layer was grown at high temperature to obtain a -GaN islands with uniform size. Subsequently, a -GaN buffer layer was deposited at 1050 °C with a high V/III ratio of 900 for the purpose of enhancing the crystal quality and surface flatness. Then, a 3- μ m-thick a -GaN epitaxial layer was successively grown with a higher lateral growth mode at a V/III ratio of 1000 at 1100 °C, followed by approximately 1- μ m-thick Mg-doped a -GaN layer. The carrier concentration and hall mobility were measured to be $1.28 \times 10^{17} \text{ cm}^{-3}$ and $3.93 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively by the Hall measurements using van der Pauwe method.

Nonpolar a -ZnCdO films were hydrothermally grown on a -GaN templates using a simple aqueous solution method. Accordingly, 30 ml of zinc nitrate hexahydrate (4.1–33 mM) and equivalent cadmium nitrate tetrahydrate (3.3–30 mM) were prepared, and mixed together in a Teflon-lined autoclave. The concentration of each solution was varied from 0.10–1.81 depending on the ratio of Cd to Zn ions in the total solution. Subsequently, 10 ml of ammonium hydroxide solution (4.4–200 mM) was added slowly to the mixed solution while stirring it. Finally, the a -GaN film substrate was suspended upside down in the nutrient solution, and placed in an oven at 80 °C for 60 min. After the growth, the sample was taken out, washed with deionized water vigorously, and blow-dried with nitrogen. This growth cycle was repeated to produce a thick a -ZnCdO film. After hydrothermal growth of a -ZnCdO, the samples were annealed at 600 °C for 1 min under oxygen ambient using rapid thermal annealing (RTA) system for the activation of Cd ions in a -ZnCdO. The van der Pauwe Hall measurement showed $4.78 \times 10^{18} \text{ cm}^{-3}$ and $14.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively for the carrier concentration and hall mobility of the n -type a -Zn_{0.957}Cd_{0.043}O film.

For the LED fabrication, Ni/Au (20/80 nm) was deposited on the p -type a -GaN using electron beam evaporation followed by RTA at 500 °C for 1 min under oxygen ambient. A mesa pattern was formed using conventional photolithography. Further, 680 nm thick a -ZnCdO was synthesized using cyclic aqueous solution method and lifted-off. Ti/Au (20/100 nm) contact was formed on the a -ZnCdO mesa as a top n -type electrode.

The surface morphology of the a -ZnCdO film was examined using Hitachi S-4300 field emission scanning electron microscope

(FESEM) and PSIA XE150 atomic force spectroscopy (AFM). The Cd content in the ZnCdO films were determined by Bruker corporation XFlash 410 energy dispersive X-ray spectroscopy (EDX). 10 different spots on the sample were measured and averaged for the Cd to Zn ratio value. The crystallographic characterization was performed using Jordan Valley QC3 high resolution X-ray diffraction (XRD) system with a Cu K α X-ray target source ($\lambda = 1.5406 \text{ \AA}$). The photoluminescence (PL) spectra of the a -ZnCdO were measured by Nanometrics RPM2000. The current-voltage (I - V) characteristics and electroluminescence (EL) of the nonpolar n -type a -ZnCdO/ p -type a -GaN heterostructure device were measured by Agilent 4155C semiconductor parameter analyzer and an on-wafer measurement system.

3. Results and discussion

Fig. 1 (a) and (b) show the SEM and AFM images of a -ZnCdO hydrothermally grown with a mixed solution of 16.5 mM ZnNO₃, 20 mM CdNO₃, and 35 mM NH₄OH at 80 °C for 60 min. Energy dispersive X-ray spectroscopy showed Zn to Cd ion ratio of 0.957–0.043 (a -Zn_{0.957}Cd_{0.043}O). As shown in Fig. 1 (a), a high-quality dense a -ZnCdO film was obtained using facile low-temperature aqueous solution method without any surfactants and seeding layers on a -GaN. In the case of hydrothermal growth of ZnO on c -plane GaN (c -GaN), the growth rate along the c -axis direction was faster than that along any other direction owing to its higher surface energy; hence, ZnO nanorods or nanowires vertically aligned parallel to the c -axis were grown [3,4,27,28]. In contrast to the ZnO growth on c -GaN, the film type of a -plane ZnO (a -ZnO) on a -GaN was observed following the Volmer-Weber growth mode [3,29]. At the initial stage of the growth, triangular prismatic ZnO islands with a -plane base grow along the c -axis direction. As the growth progresses, individual ZnO prisms coalesce together with adjacent prisms and form a continuous nonpolar a -ZnO film. By adding Cd ions to the growth solution, the length of the grain along the c -axis was reduced, but a similar growth behavior was observed in a -CdZnO. The AFM image of hydrothermally grown a -Zn_{0.957}Cd_{0.043}O on a -GaN is shown in Fig. 1 (b). A distinctive striated surface morphology along the c -axis direction was not observed, but the root-mean-square (RMS) roughness over a scan range of $5 \times 5 \mu\text{m}^2$ was 24.74 nm, which is less than that of hydrothermally-grown pure a -ZnO film on a -GaN substrate (67.97 nm) [3].

The optical and structural properties of a -ZnCdO films on a -GaN with various Cd contents were investigated. The dependences of peak wavelengths in PL and intensity ratios of a -ZnCdO peak to a -GaN in XRD on the percentages of Cd contents are shown in Fig. 2(a) and (b), respectively. The peak wavelengths in PL as a function of the intensity ratios of a -ZnCdO peak to a -GaN in XRD are shown in Fig. 2(c). All the samples were annealed at 600 °C for 1 min under oxygen ambient using the RTA system for the activation of Cd ions in a -ZnCdO. As illustrated in Fig. 2(a), the peak wavelengths in PL increase with the Cd content in a -ZnCdO. The peak wavelength of pure a -ZnO in PL was 377 nm (3.29 eV) [7],

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