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Comparative study of the ZnO and $Zn_{1-x}Cd_xO$ nanorod emitters hydrothermally synthesized and electrodeposited on *p*-GaN

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ABSTRACT

Hydrothermal synthesis and electrodeposition are low-temperature and cost-effective growth techniques of high quality nanostructured active materials for opto-electronic devices. Here we report a hydrothermal seed layer-free and rapid synthesis (15 min) of epitaxial nanorod arrays of ZnO on *p*-GaN(0 0 0 1). The effects of hydrothermal (HT) versus electrochemical deposition (ECD) synthesis on the optical properties of ZnO nanorods/nanowires on *p*-GaN substrate are compared in details. For both types of layers, a strong photoluminescent UV-emission was found indicating the high quality of the synthesized ZnO layer. The hetero-structures were used for LED applications. With HT-ZnO and ECD-ZnO, UV-emission started at remarkably low forward voltage of 3.9–4.0 V and 4.4 V respectively and increased rapidly. Moreover, the LED structures showed a stable and repeatable electroluminescence. We propose for further studies a simple, efficient, seed layer-free and low temperature hydrothermal growth technique to fabricate high quality ZnO nanorods/*p*-GaN heterojunction LED nanodevices. It is also demonstrated that a single short wavelength emission can be shifted to the violet range with Cd-alloying of ZnO used for LED structure.

1. Introduction

The development of efficient short-wavelength light emitting diodes (LEDs) has attracted much attention in the last few years. Near-UV and violet-blue sources can be combined with efficient phosphors for solid-state lighting to replace traditional lamps due to their characteristics of long lifetimes and energy saving [1,2]. There exists an increasing demand for LEDs in automobiles headlights, street lighting, back-lighting for display and so on. Nowadays, InGaN- and GaN-based LEDs are under intense research [3]. However, ZnO is a promising alternative emitting material due to many advantageous properties such as a direct bandgap at 3.37 eV, a large exciton binding energy of 60 meV at room temperature and nanostructuration [4–7]. Heterojunction of *n*-ZnO/*p*-GaN for light emitting devices is one of the best candidates for near-UV LEDs, if we consider a large variety of promising results reported in the literature [4–11]. In particular, the devices based on ZnO-nanorods/*p*-GaN-thin films heterostructures are interesting due to the possibility of improved light extraction from nanorod-based devices. Also, the potential for cost-efficient fabrication of ZnO based devices is very attractive. With ZnO nanotips perpendicularly grown on transparent *p*-GaN-LEDs by metal–organic chemical vapor deposition (MOCVD), the light output power of such LEDs was improved by 1.5–1.7 times compared with conventional ones [8–11]. However, current techniques, such as MOCVD, are applied at elevated temperatures to synthesize high quality ZnO nanorods/nanotips, that may degrade the ohmic contact with *p*-GaN and result in significantly increased forward bias of GaN-LEDs [8]. In addition, the quality of *p*-GaN:Mg will be affected by Mg-dopant activation during the high-temperature process. To avoid these disadvantages, cost-effective, low-temperature electrochemical or aqueous solution methods for growing zinc oxide nanorods on *p*-electrode of GaN-LEDs was recently demonstrated [4–6,12,13]. The effect of different growth regimes, which affect the density of zinc oxide nanorod arrays and respectively the light extraction efficiency, was also experimentally investigated [4,5,12–14]. High-density nanorod arrays were proved to be able to

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extract much more light out of GaN-based LEDs than lower density nanorod arrays. Directional output behavior of the GaN-based LEDs with hydrothermal synthesis (HT) and electrochemical deposition (ECD) ZnO nanorod arrays was also observed [12–14]. However, in previous papers on HT-ZnO the reported threshold voltage was usually about 10 V [13] and the best experiments gave a threshold voltage of about 5 V [15–17]. In this study, we have investigated the influence of the hydrothermal synthesis versus electrochemical deposition on the optical properties of ZnO/*p*-GaN LEDs.

Hydrothermal synthesis of nano-ZnO is an efficient and green procedure of ZnO nanorod growth on many types of surfaces. Electrochemical deposition (ECD) has become an important technique for fabricating ZnO nanowire-based heterojunctions due to its simplicity, cost-efficiency, large-area deposition and good-quality nanorod arrays [4,18–21]. Hydrothermal and electrochemical are both low temperature solution growth techniques. As was proven before [4–6], an improved heterostructure is expected when GaN is used. ZnO and GaN both have the same wurtzite hexagonal structure, similar lattice parameters, a small in-plane lattice misfit constant (~1.8%),[21] the same stacking sequence (2H) [22], a strong exciton binding energy of 60 meV for ZnO compared to 25 meV for GaN that would favor light emission at room temperature from zinc oxide [4,5,14,23]. Our previous reports on the hydrothermal synthesis technique of ZnO nanorods will serve as a reference for this work [24–26]. In this report, we present the adapted growth conditions, which give the desired ZnO nanorods dimensions on *p*-GaN surface and improved optical quality to achieve high light extraction. The results are compared to our previously reported ECD ZnO-NR/NW layers grown on *p*-GaN. In premiere for hydrothermal synthesis it was demonstrated that a single short wavelength emission can be shifted in the violet range with Cd-alloying of ZnO used for LED structure.

2. Experimental details

The ZnO nanorod arrays on *p*-GaN substrates were grown hydrothermally according to a procedure described elsewhere in our previous papers [24–27]. The *p*-type substrate was a commercial magnesium-doped GaN(0 0 0 1)-oriented layer grown on sapphire with the *c*-axis perpendicular to the substrate (TDI, Inc. Corporation). The GaN layer was ~2.5 μm thick, with a crystal miscut of ~0.59° and a dopant concentration of $4 \times 10^{18}\,\mathrm{cm}^{-3}$. Before ZnO deposition, the *p*-GaN(0 0 0 1) substrate was degreased in trichloroethylene at 50 °C for 12 min, subsequently cleaned 6 min in acetone at 52 °C and 8 min in methanol at 22 °C both under ultrasonic and then rinsed with deionized water. Next, the substrate was etched 10 min in concentrated ammonia (27%) at 58 °C, subsequently etched in HCl:H_2O (1:1 vol.) for 15 min to remove any native oxide [5,26–28] and finally rinsed with high purity water (resistivity of 18.2 MΩ cm). This procedure was described in Ref. [5] and was used to clean these *p*-type substrate surfaces.

Zinc sulfate [$Zn(SO_4)\cdot 7H_2O$] and ammonia (NH_4OH) (Fisher Scientific, reagent grade, without further purification) were used for the synthesis of ZnO nanoarchitectures. 0.10–0.15 M $Zn(SO_4)\cdot 7H_2O$ and 2 M ammonia solution NH_4OH (29.6%) were mixed with 100 ml DI–water until complete dissolution at 22 °C and it became colorless [24,27]. Afterwards, the *p*-GaN substrates were placed inside an aqueous solution in a reactor described in our previous papers [24–27]. The set-up was mounted on a hot plate, and the temperature was quickly increased to 95–98 °C and kept constant for 15 min without any stirring. Manipulation and reactions were carried out inside a fume hood. For one set of samples $CdCl_2$ (Alfa Aesar) was added in the bath at 8 μM to perform doping. All samples were exposed to post-deposition annealing at 300 °C in air for 20 min. The as-prepared and thermally processed ZnO NR arrays were characterized by X-ray diffraction (XRD) using a Rigaku 'D/B max' X-ray diffractometer equipped with a monochromatized CuK_α radiation source (λ=1.54178 Å). The operating conditions were 30 mA and 40 kV at a scanning rate of 0.02°/s in the 2θ range from 25° to 130°. Data acquisition was made with the software Data Scan 3.1 and analyzed with Jade 3.1 (from Materials Data Inc.). The morphology was studied using a VEGA TESCAN TS 5130MM scanning electron microscope (SEM). The different characterization techniques confirmed that the nanorod arrays were highly crystalline with regular rods distributed throughout the substrate surface. This morphology is considered to play a major role in nanodevice applications.

The micro-Raman spectra of the ZnO-NW arrays were measured using a Horiba Jobin-Yvon LabRam IR system in a backscattering configuration. The 632.8 nm line of a He–Ne laser was used for off-resonance excitation with less than 4 mW power at the sample. The continuous wave (cw) photoluminescence (PL) was excited by the 325 nm line of a He–Cd laser by Melles Griot. The emitted light was collected by lenses and was analyzed with a double spectrometer providing a spectral resolution better than 0.5 meV. The signal was detected by a photomultiplier working in the photon counting mode. The samples were mounted on the cold station of a LTS-22-C-330 optical cryogenic system. The LED device, integrating the ZnO-NR/*p*-GaN heterostructure, was maintained by a bulldog clip and was biased with a Keitley 2400 source [5]. Its electroluminescence (EL) was collected by an optical fiber connected to a CCD Roper Scientific detector (cooled Pixis 100 camera) coupled with a SpectraPro 2150i monochromator. The monochromator focal lens was 150 mm, grating of 300gr/mm blazed at 500 nm in order to record the emission of the ZnO in the whole near-UV–visible range.

3. Results and discussions

Fig. 1(a) shows a side-view of the close-packed ZnO NRs hydrothermally grown on the (0 0 0 1) *p*-type GaN substrate. Their mean radius is 180 nm and the rods have a flat top. It can be distinguished a heterostructure *n*-ZnO NRs/*p*-GaN/sapphire, which is used in LEDs. Also, in Fig. 1(a) we can observe that the ZnO/GaN interface is smooth and the nanorods are perpendicular to the *p*-GaN layer. A top view of the ZnO nanorod arrays hydrothermally grown on the *p*-type GaN substrate is presented in Fig. 1(b). On the top view, one can observe the hexagonal section of the NRs with a dense morphology. The lateral facets are oriented in the same direction for the various NRs (Fig. 1(b)) and the top aspect is typical of an epitaxial growth with all the NRs having the same in-plane crystallographic orientation [29,30]. No changes in SEM images were observed for the *n*-$Zn_{1-x}Cd_xO$ NRs/*p*-GaN:Mg. The *n*-type ZnO is epitaxially grown directly on the (0 0 0 1) *p*-type GaN:Mg.

The $\theta/2\theta$ XRD pattern of the heterostructure (*n*-ZnO NRs/*p*-GaN) is dominated by both ZnO and GaN reflection peaks (Fig. 2). Single crystalline GaN film is oriented with the *c*-axis perpendicular to the sapphire substrate. On the enlarged view (Fig. 2(b)), we observe the ZnO(0 0 0 2) diffraction peak on the left-side of GaN(0 0 0 2) reflection. Fig. 2(c) shows the enlarged views of the ZnO(0 0 0 4) peak on the left-side of the GaN(0 0 0 4) reflection. XRD data confirm that GaN and HT-ZnO have the same out-of-plane orientation. The patterns are typical of a perfectly textured ZnO material. The full width at half maximum of (0 0 0 2) peak for ZnO and GaN are the same at 0.07° and close to the apparatus line width. The value is typical of a very high quality well-crystallized heterostructure. The rods are very well-crystallized with a large size (radius measured at about 180 nm, each rod being a single crystal). From XRD (not shown) it was observed a slight lattice deformation/expansion for Cd-ZnO NWs due to these differences in ionic radii ($r(Zn^{2+})$ = 0.074 nm,) by Cd ($r(Cd^{2+})$ = 0.095 nm). The lattice constants for our samples *a* and