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Fabrication of ZnO nanorod/*p*-GaN high-brightness UV LED by microwave-assisted chemical bath deposition with $Zn(OH)_2$–PVA nanocomposites as seed layer

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ABSTRACT

Chemical solution deposition is a low-temperature and possibly the lowest-cost method of growing ZnO nanorods on a GaN substrate. However, most reported methods leave an interface layer between the grown ZnO nanorods and substrate, which can interfere with light emission and extraction. Here we report the growth of high-quality, vertically aligned ZnO nanorods directly on a *p*-type GaN substrate, with no interface layer, by microwave-assisted chemical bath deposition using a polyvinyl alcohol (PVA)–$Zn(OH)_2$ nanocomposites as the seed layer. X-ray diffraction and field-emission scanning electron microscopy confirmed the high quality of the nanorods in addition to the narrow and high-intensity UV peak of the photoluminescence spectrum. Three different filling insulator materials, poly methyl methacrylate (PMMA), SiO_2, and PVA, were used to fabricate *n*-ZnO nanorod/*p*-GaN thin film LED structures. The electroluminescence (EL) properties for these three devices showed different emission peaks, which mainly originated from the recombination of free carriers at the two sides of the heterojunction. All devices showed excellent LED performance under forward and reverse bias; the PMMA device showed EL peaks in the UV–blue region, and the SiO_2 device displayed EL peaks in the UV and green regions, respectively.

1. Introduction

Solid-state light emitting devices have drawn considerable research attention due to their low power requirements compared with conventional devices. One-dimensional zinc oxide (ZnO) nanostructures, in particular, are very promising for optoelectronic applications owing to their unique properties and wide band gap (3.37 eV) as well as high exciton energy (60 meV) [1,2]. Furthermore, ZnO is an efficient emitter in the blue and ultra-violet (UV) region [3,4]. As synthesis, ZnO show the *n*-type conductivity due to native defects related to oxygen vacancy, zinc interstitial, unintentionally H doping, and other structural defects [5–8]. The fabrication of ZnO homojunction devices, however, is impractical because of the instability of the *p*-type material. This motivated a search for other *p*-type materials [9,10] such as GaN [9–36], CrO_3 [3], Si [37], and some *p*-type polymers [38–40]. Among these materials, GaN shares the same wurtzite hexagonal structure and lattice parameters as ZnO, with a small lattice mismatch (1.9%), which makes GaN a good substrate for epitaxial growth of ZnO nanorods [41]. In addition, epitaxial growth of nanostructured ZnO on GaN has the further advantage of providing a small-area junction in which nanorods act as waveguides that work as an internal lens and path for the emitted light [42]. Moreover, the nanorods have few grain boundaries and defects compared with thin films [43].

To date, various methods have been developed to grow nanostructured ZnO on GaN: metalorganic vapor deposition (MOCVD) [36], chemical vapor deposition [9,44], pulse laser deposition [17], molecular beam epitaxy (MBE) [45], atomic layer deposition (ALD) [32], RF sputtering [27], electrochemical deposition [46], and aqueous chemical deposition [12,43,47–49]. Recently, researchers have shown an increased interest in chemical solution deposition due to its low temperature and the fact that it involves the lowest cost for the growth of ZnO nanorods on a GaN substrate. These synthesis methods employ different seed layers such as spin-coated and RF-magnetron-sputtered ZnO [50,51]. However, this leaves an interface layer between the grown nanorods and the substrate, which will affect the light emission and extraction from the device.

This paper proposes a method of growing ZnO nanorods using a nanocomposites material as a seed layer such that there is no interface layer left between the grown ZnO nanorods and the substrate. In the present work, microwave irradiation was used for superheating in a chemical solution deposition method using

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nanocomposites as the seed material. The seed material comprised a complex of zinc ions with poly (vinyl alcohol) (PVA) placed on the GaN substrate prior to the growth of ZnO nanorods.

2. Experimental details

2.1. Growth of ZnO nanorods on p-type GaN wafer

P-type GaN thin film (7.6 μm) deposited on a sapphire substrate (3-inch diameter) by hydride-vapor phase epitaxy (HVPE) was purchased from TDI Oxford Instruments Company (UK). The hole concentration was measured (by the company) on a satellite wafer by a mercury probe on the basis of capacitance–voltage characteristics. For this wafer, (Na–Nd) was estimated at $2–3 \times 10^{18}$. Prior to the epitaxial growth of the ZnO nanorods, the GaN substrate was cleaned using a suitable procedure. The synthesis of ZnO nanorods followed our previous procedure [52,53]. In brief, the substrate (1 cm × 1 cm) was spin-coated with PVA–$Zn(OH)_2$ nanocomposites, which was prepared by complexing zinc ions with the OH groups of PVA. Then this substrate was annealed at 210 °C for 1 h to decompose $Zn(OH)_2$ to ZnO; the temperature was then elevated to 380 °C for 2 h. After annealing, the substrate was inserted vertically in a beaker containing 0.1 mol/L of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and an equal molar concentration of hexamethylenetetramine ($C_6H_{12}N_4$) dissolved in DI water. The unclosed beaker then placed inside a microwave oven (2.4 GHz) for 2 h at 90 °C, which supply a homogenous superheating to the regents. Finally, the nanorods grown on the substrate were washed with hot ethanol to remove the remaining salt. Field-emission scanning electron microscopy (FESEM) (model Leo-Supra 50VP, Carl Zeiss, Germany) determined the surface morphology of the ZnO nanorods. X-ray diffraction (XRD) (PANalytical X'Pert PRO MRD PW3040, Almelo, The Netherlands) determined their structure, orientation, and the azimuthal properties. Optical properties were measured at room temperature by photoluminescence and Raman spectroscopy (Jobin Yvon Horiba HR 800 UV, Edison, NJ, USA). The electroluminescence measurement was done using a USB 4000 (Ocean Company) at room temperature with a Keithley 2400 as the current supply.

2.2. Fabrication of ZnO nanorod/GaN heterostructure

LED devices with the structure shown in Fig. 1 were fabricated as follows: prior to the growth of ZnO nanorods on the *p*-GaN substrate, 5- and 200-nm-thick layers of Ni and ITO were deposited, respectively, by RF-sputtering on the *p*-GaN substrate, followed by annealing at 350 °C for 1 h under nitrogen ambient. After the growth of ZnO nanorod arrays, poly methyl methacrylate (PMMA), thin layer of SiO_2 (deposited by RF sputtering), and PVA were used as filling materials to ensure that all spaces between the nanorods were filled and thus prevent a short circuit between the top contacts (*n*-type ITO) with the substrate. The fabricated devices that coated by PMMA, SiO_2, and PVA are denoted as device A, B, and C, respectively.

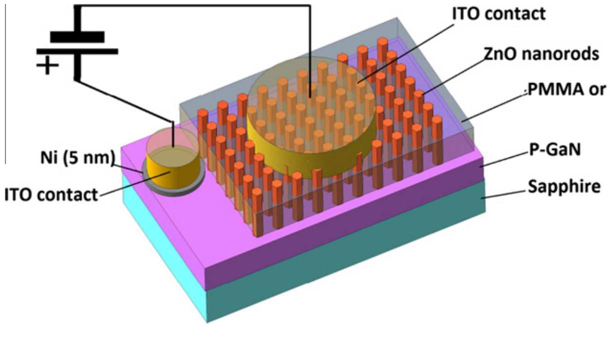

Fig. 1. Schematic illustration of fabricated *n*-type ZnO nanorods/*p*-type GaN thin film LED.

Device A was also subjected to an oxygen plasma for 5 min at 100 W power to remove the small amount of PMMA from the top of the ZnO nanorods, while device C was dipped in DI water for one time. Finally, the ITO thin film was deposited on the ZnO nanorods in all devices to form the *n*-type contact as well as light-emitting window.

3. Results and discussion

3.1. Characteristics of epitaxial ZnO nanorods

As seen in Fig. 2a, the XRD pattern shows the hexagonal wurtzite structure of the ZnO nanorods, with strong diffraction intensity peaks related to the (0002) plane of the ZnO nanorods ($2\theta = 34.43°$) and the GaN substrate ($2\theta = 34.52°$). The high diffraction intensity of these two peaks suggests that the ZnO nanorods and GaN substrate form an excellent-quality heterojunction with superior orientation toward the (0002) plane. X-ray Rocking curve was conducted using triple axis ω-2θ configuration to investigate the quality of the hetro-epitaxy ZnO nanorod arrays on GaN substrate. Fig. 2b shows the ω-2θ scan for ZnO nanorod arrays on GaN substrate, which display very narrow peak consists of two overlapped peaks related to the (0002) orientation of ZnO and GaN. The FWHM of this peak is equal to 0.186°, which indicted the well-oriented *c*-axis with high quality epitaxial growth of ZnO nanorod arrays on GaN substrate. Moreover, X-ray azimuthal ϕ-scan was carrying out for ZnO nanorod arrays on GaN substrate at a high diffraction angle ($2\theta = 107.53°$ and $\psi = 42.77°$) for the {204} reflections of ZnO, which can be distinguished from the reflections of {204} for GaN substrate at $2\theta = 109.17°$. Fig. 2c shows the ϕ-scan for ZnO nanorod/GaN, and GaN substrate, which reveal the six peaks related to the sixfold symmetry of ZnO and GaN. This result indicates that ZnO nanorods aligned vertically on GaN substrate, which proves the epitaxial growth of the ZnO nanorods on GaN [54].

The morphology of the nanorods, as seen in the FESEM image of Fig. 3a, revealed a hexagonal structure and regular vertical alignment. In addition, the ZnO nanorods have high-growth distribution density on the GaN substrate, which is related to the good homogeneity of the seed layer. The FESEM image of the nanorods on device A after oxygen plasma etching, as in Fig. 3c, shows the tips of the nanorods and the PMMA filling the space between the nanorods. For device B, the FE-SEM cross-sectional view (Fig. 3b) indicates the absence of an interface layer formed from the seeding layer, and one can notice that the ZnO nanorods were grown directly from the substrate surface [53]. The optical properties of the nanorods was examined at room temperature by photoluminescence (PL) spectroscopy, where the PL spectra was excited by a He–Cd laser ($\lambda ex = 325$ nm). As shown in Fig. 4, the dominant peaks observed in the UV region (378 nm for ZnO and 363 nm for GaN) are attributed to the near-band-edge UV emission (NBE) of the wide-bandgap ZnO nanorods and GaN, which results from the recombination of free excitons [9]. The sharp (FWHM = 13 nm) and high-intensity UV peaks, compared with the weak spectral bands in the visible region, indicated that the ZnO nanorods and *p*-GaN have high quality hexagonal structures with low structural and surface defects [17]. In other words, the high ratio of the UV intensity peak to the visible intensity peak (I_{UV}/I_{Vis}) for ZnO nanorods is the main identifying feature of high-quality ZnO [55]. In addition, one can note from the PL spectrum of *p*-GaN the absence of blue emission due to transition between the conduction band