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Letter

ZnO interconnected network nanostructures grown on cracked GaN by the aqueous solution method

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ABSTRACT

ZnO interconnected network nanostructures are grown on cracked GaN substrate using aqueous solution method in this paper. ZnO nanostructures nucleate in the sidewall of crack and selectively grow along the crack direction on the GaN substrate. Due to the diversity of the crack, the nanostructures show interconnected network structures. Time-dependent of ZnO nanostructure morphology evolution shows the network nanostructures are formed by self-organized growth by interconnection of nanorods. The average diameter of the nanorods is around 500–600 nm. Micro-Raman spectroscopy shows the nanostructures are under tensile stress. Meanwhile, the nanostructures also show good optical quality. The interconnecting structure characteristics, high degree of networking make them potential applications in ultra-sensitive gas sensing, exciton based photonic devices.

1. Introduction

ZnO-based nanoscale materials, as important functional oxide nanostructures, have received increasing attention over the past few years due to their potential applications in optoelectronic switches, high-efficiency photonic devices, near-UV lasers, and assembling complex three-dimensional nanoscale systems [1–5]. Since the surfaces and morphologies of the ZnO nanostructures play a crucial role in their nonlinear optical properties [6]. There are many reports of synthesizing many interesting nanostructures of ZnO [7–9]. Meanwhile, because ZnO and GaN have the same wurtzite crystal structure and low lattice misfit of 1.9%, many methods have been used to produce ZnO nanostructures on GaN substrates, such as thermal evaporation, catalyst-assisted vapor liquid solid (VLS), laser ablation, metal-organic chemical vapor deposition (MOCVD), and template-assisted and solution processes [10–12]. In addition to the above methods, solution-based chemical approach has been demonstrated to be very efficient in synthesizing single crystal structure at a remarkably low temperature [13,14]. Recently, several groups reported the ZnO nanostructures grown on GaN and demonstrated the potential to realize photonic and electronic devices [15–17]. Dalui reported on the fabrication of n-ZnO nanorod arrays vertically grown on p-GaN and demonstrated the potential to realize photonic and electronic nanodevices [18,19]. Generally, the ZnO nanostructures grown on GaN by aqueous solutions are vertically randomly distributed nanorods [20–22]. To control the size and site of ZnO nanostructure always need nanopatterned templates to utilize the selective nucleation and direct the growth.

In this paper, we report novel ZnO nanostructures grown on cracked GaN by aqueous solution method. The crack of GaN on Si(1 1 1) directs ZnO horizontal nucleation and vertical growth along the crack direction. Due to the diverse orientation of the crack from the GaN substrate, the nanostructures show network structure. Time-dependent of ZnO nanostructures morphologies evolution shows the network nanostructures are formed by self-organized growth by interconnection of nanorods. The average diameter of the nanorods is around 500–600 nm. Micro-Raman spectra shows the nanostructures are under tensile stress. The interconnecting structure characteristics, high degree of networking and high surface area of these unique nanostructures make them potential applications in ultra-sensitive gas sensing, exciton based photonic devices.

2. Experimental

The GaN template was grown on n-type Si(1 1 1) substrates by low pressure (LP) MOCVD in a vertical reactor with a high speed rotation disk holder for multiple wafers. Trimethylgallium (TMGa), trimethylaluminum (TMAl) and high purity ammonia (NH_3) were used as Ga, Al and N precursors, respectively, with H_2 as carrier gas. The structure is consisted of a 30 nm AlN layer, 1 μm thick undoped GaN layer. Before growth in the aqueous solution, the GaN substrate was cleaned in the deionized water, ethanol, and acetone. All chemical reagents in the experiments were of analytical grade (AR) and used without further purification. In a typical experiment

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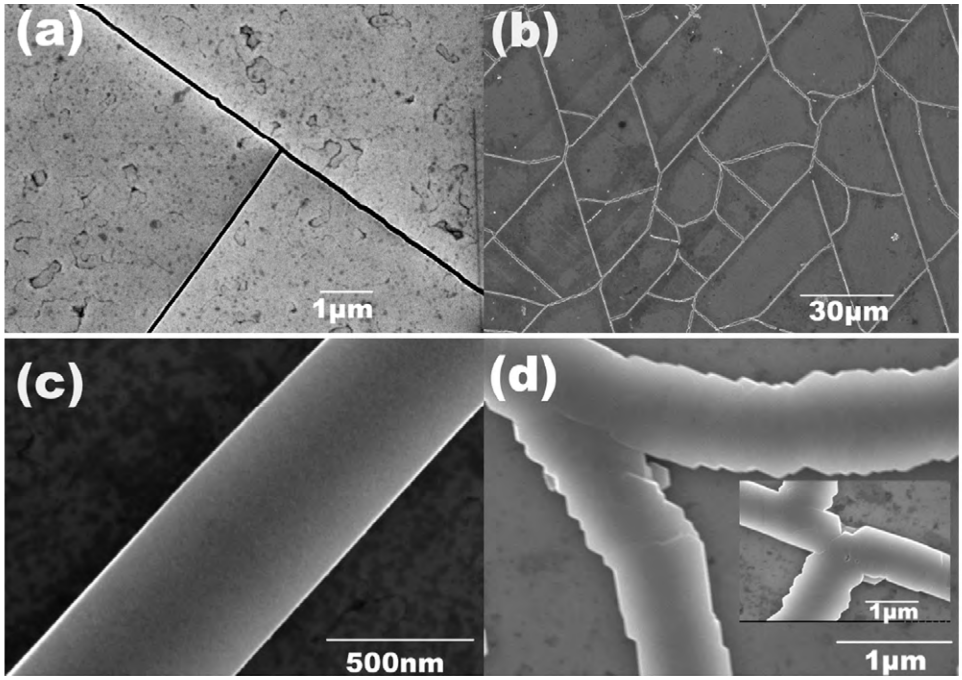

Fig. 1. (a) Top-view SEM of cracks for GaN grown on Si(1 1 1), (b) top-view SEM images of nanostructures on cracked GaN. (c and d) Magnification of networks structure, the inset displays the connection of nanostructures.

an equimolar (0.05 M) aqueous solution of zinc nitrate ($Zn(NO_3)_2$) and hexamethyltetramine ($C_6H_{12}N_4$) was prepared. The GaN substrate was putted into the above solution of 95 °C for 2 h. After deposition, the sample was cleaned with deionized water and then dried in an air atmosphere. Similarly, another five samples were also obtained by different growth time.

Field emission scanning electron microscopy (FE-SEM Hitachi S-4800), and energy-dispersive X-ray spectroscopy (EDS) attached to the SEM were used to investigate the morphology, and composition of the as-grown ZnO network nanostructure. Based on the EDX measurement, the spatial distribution of Zn, O, and Ga is analyzed by the element mapping technique. Room temperature photoluminescence (PL) was performed using ACCENT RPM4000 with excited wavelength of 266 nm laser as the excitation source with resolution of 0.5 nm. Micro-Raman spectra were measured with confocal Raman spectroscopic system (Renishaw 2000, Invia). The 632.8 nm radiation from the He–Ne laser was used as an exciting source.

3. Results and discussion

Fig. 1(a) displays the SEM morphology of GaN grown on Si(1 1 1) with 2 h growth time, the appearance of cracks along the $\{1\,-1\,0\,0\}$ in the GaN layers grown on the Si substrate, the diameter of crack is around 100 nm. Cracks in GaN on Si are known to be formed during the cooling stage due to a large tensile stress caused by the

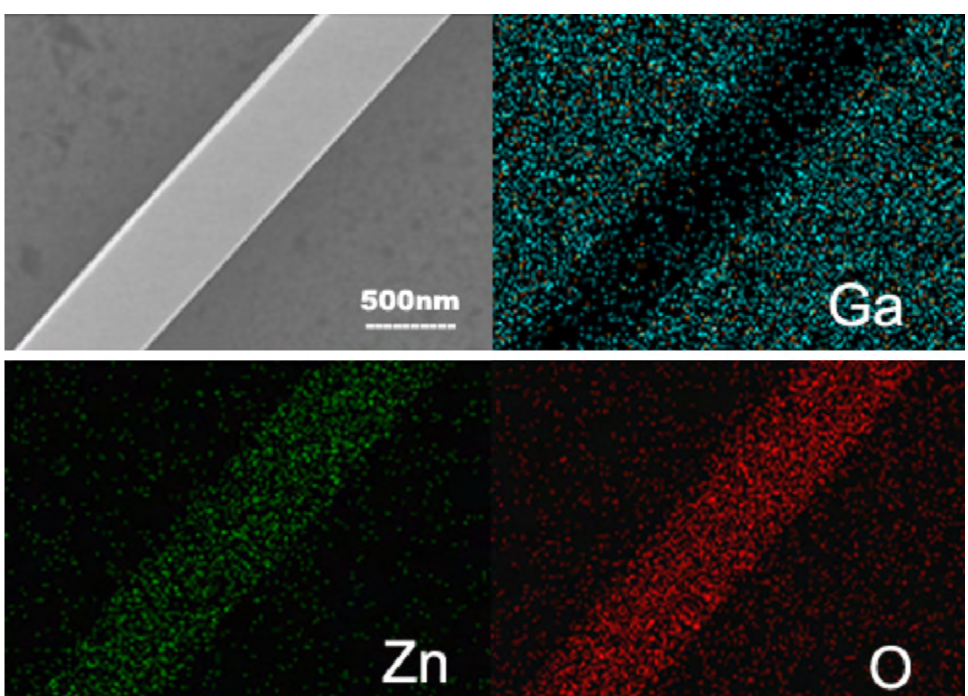

Fig. 2. EDX elemental mapping of nanorod; (b), (c), (d) is the intensity of each element corresponding Ga, Zn, O respectively.

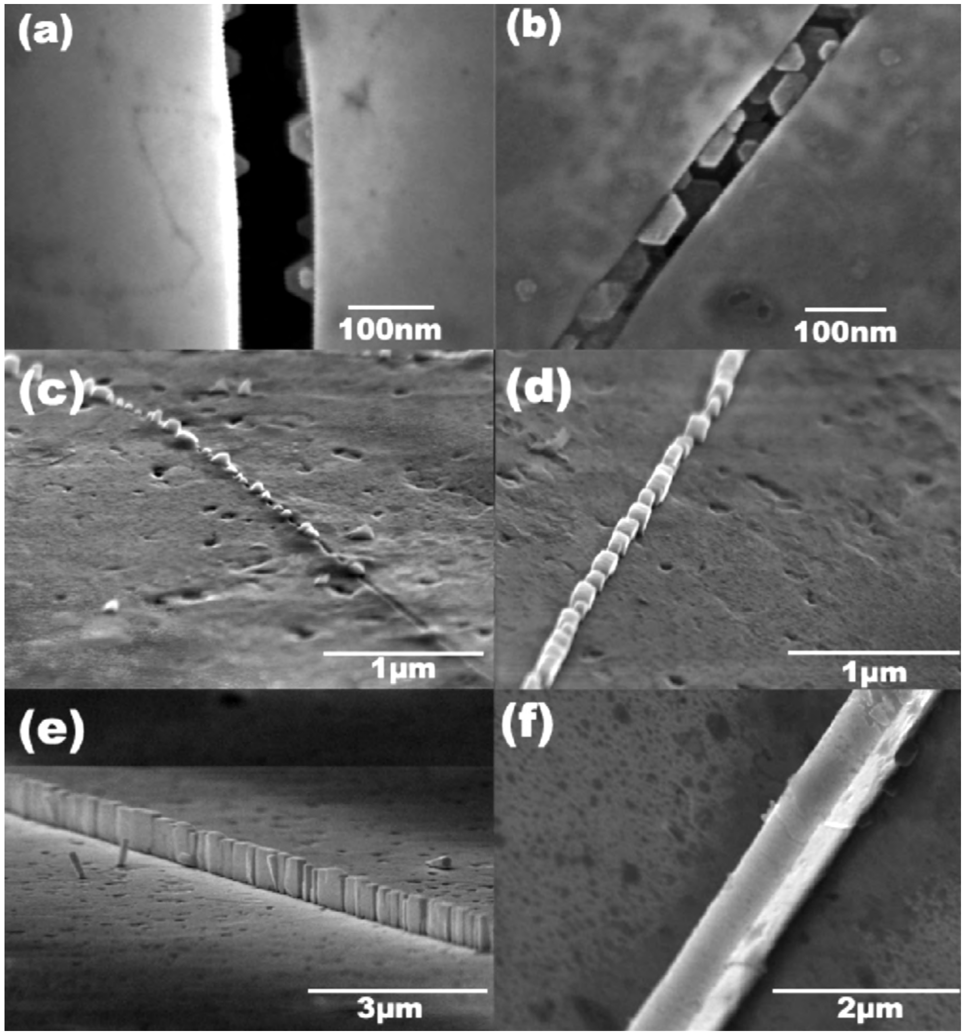

Fig. 3. Time-dependent of ZnO nanostructure morphology evolution: (a) 6 min, (b)12 min, (c) 25 min, (d) 40 min, (e) 1.0 h, and (f) 2.0 h.

large difference in thermal expansion coefficients [23,24]. Fig. 1(b) shows the top-view SEM image of the samples after growth. It can be clearly seen the interconnected network arrays are formed by growth along the crack of GaN substrate. Due to the diverse orientation of the crack from the GaN substrate, the nanostructures show networks structure. Meanwhile, the distribution of the nanostructures is fairly uniform throughout the entire substrates along the crack. Fig. 1(c) and (d) is the magnification of networks structure. Fig. 1(d) inset displays the connection of nanostructures. The networks structure is mainly composed by horizontal high aspect ratio nanorods interconnecting with arc-shaped ZnO nanorods. The average diameter is around 500–600 nm.

The evidence for the synthesis of the ZnO nanostructures can be proved by energy-dispersive X-ray (EDX) spectra. EDX element maps were collected by scanning the nanorod region. (Fig. 2(a)). Fig. 2(b), (c), and (d) shows the images of each element corresponding to Ga, Zn, and O, respectively. It is clear that the presence of Zn and O is uniform along the nanorod. The elemental mapping confirms that ZnO is formed along the cracked GaN substrate.

Fig. 3 displays the ZnO nanostructures morphology evolution with different growth time. The formation of ZnO nanostructures in the solution involves three processes: the horizontal nucleation in the sidewall of crack and vertical growth along the crack direction, then nanostructures are formed by self-organized growth through interconnection of nanorods. Fig. 3(a) and (b) presents top-view of ZnO nanostructure with growth time for 6 min and 12 min respectively. It indicates ZnO nanocrystals nucleate on the crack sidewall in the initial stage. Fig. 3(c) and (d) shows the oblique view of the ZnO growth with time 25 min and 40 min, ZnO crystallites nucleate along the *c*-axis and grow into 1D nanorods based on surface energy minimization. Fig. 3(e) and (f) is the oblique view of the ZnO of the ZnO growth with time 1 h and 2 h, it can be clearly seen, the nanorods grow along the crack direction and form the nanostructures by the interconnection of the nanorods.

Fig. 4 presents the typical micro-Raman spectrum of ZnO nanostructures at the range of 250–650 cm^{-1}. It was taken in the backscattering configuration at room temperature. The dominant peak at 520 cm^{-1} is attributed to Si substrate. According to the selection rule of the photon mode in hexagonal wurtzite-structure ZnO, the peak at 436.1 cm^{-1} is assigned to the high frequency E_2 photocharacteristic. The 300.5 cm^{-1} mode is ascribed to the multiple-photon scattering process in the hexagonal wurtzite structure crystals [25]. The other peaks at 562.6 cm^{-1} and 732.2 cm^{-1} corresponded to E_2 (high) and A_1 (LO) photon mode of GaN, which is in agreement with selection rules. Huang et al. have demonstrated that the stress induced in crystal would obviously affect the E_2 (high) phonon frequency respectively [26]. Previous works show that an increase in the E_2 (high) photon frequency is ascribed to compressive stress, whereas a decrease in the E_2 (high) photon frequency is ascribed to tensile stress. GaN suffers tensile stress whose E_2 (high) is smaller than strain-free crystal sample value of 567.2 cm^{-1}[27]. Meanwhile, it has been

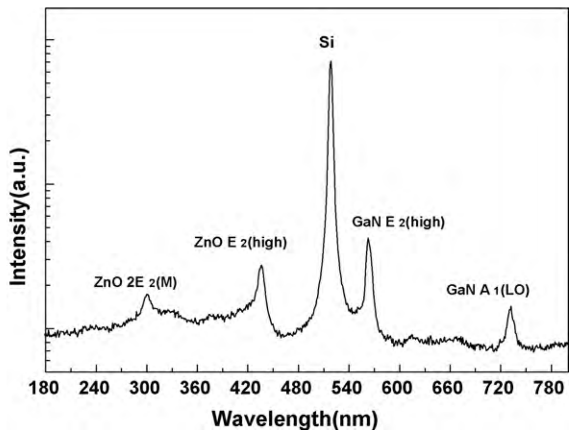

Fig. 4. Typical micro-Raman spectra of ZnO nanostructures.

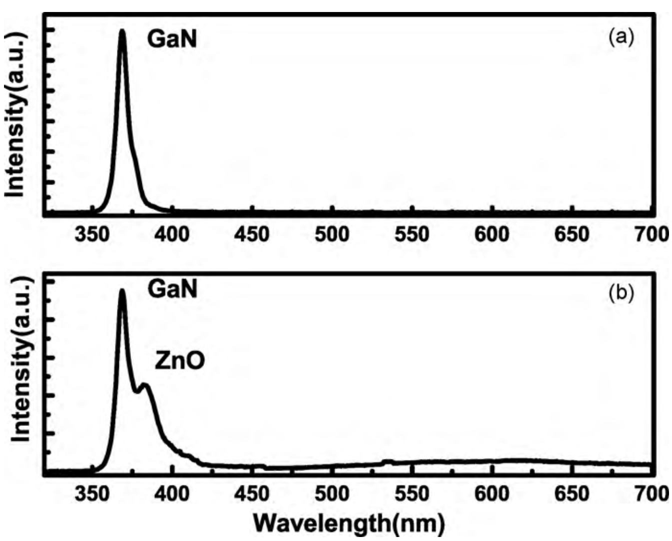

Fig. 5. Typical PL spectra of GaN template and ZnO nanostructures/GaN using 266 nm laser as a source excitation.

reported that the E_2 (high) mode of GaN shifts linearly with stress with 2.9 cm^{-1}/GPa for biaxial stress [27]. The tensile stress calculated is 1.58 GPa. For the ZnO nanostructures grown on GaN, the E_2 (high) mode is at 436.1 cm^{-1}, which downshifts in comparison with the stress-free bulk ZnO value of 437 cm^{-1} [28], indicating that the ZnO nanostructures suffer from a tensile stress. The correlation between the Raman shift and the stress can be simply expressed as $\Delta\omega\,(cm^{-1}) = 4.4\sigma$ (GPa) [28]. According to this formula, the tensile stress of ZnO nanostructures is 0.2 GPa.

Fig. 5 shows the typical room temperature PL spectra of GaN template and ZnO nanostructures under the excitation of a 266 nm laser. The PL spectrum of GaN template before ZnO nanostructures growth is shown in Fig. 5(a). The template exhibits a sharp peak band edge at 367 nm. Fig. 5(b) shows the PL spectrum of ZnO nanostructures grown on GaN, the PL spectrum contains UV band peaking at 382 nm and a very weak broad green band besides the peak from GaN epilayer. The UV emission is originated from excitonic recombination corresponding to the band-edge emission of ZnO. The UV emission is originated from excitonic recombination corresponding to the band-edge emission of ZnO and the green one is related to the defects in ZnO such as oxygen vacancies [29]. The strong UV and weak green bands imply good crystal quality and low concentration of defects in the ZnO network nanostructures.

4. Conclusions

In summary, we have demonstrated ZnO interconnected network nanostructures grown on GaN substrate in aqueous solutions. The crack of GaN directs ZnO horizontal nucleation and vertical growth along the crack direction after nucleation. Due to the diverse orientation of the crack from the GaN substrate, the nanostructures show interconnected network structure. Time-dependent of ZnO nanostructure morphology evolution shows the network nanostructures are formed by self-organized growth through interconnection of nanorods. Micro-Raman spectra shows the nanostructures are under tensile stress. Meanwhile, the as-grown ZnO nanostructures also show good optical quality. The interconnecting structure characteristics, high degree of networking and high surface area of these unique nano-networks make them potential applications in ultra-sensitive gas sensing, exciton based photonic devices.

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