文章编号：1001－9014(2017)06－0646－04

DOI:10.11972/j.issn.1001－9014.2017.06.002

Preparation and characterization of Eu^{2+}-doped GaN luminescent nanofibers by electrospinning method

CHEN Yu[1,2], WEI Xue-Cheng[1], LIU Hong-Wei[3*]

(1. State Key Laboratory on Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China;
2. Guangxi Key Laboratory of Precision Navigation Technology and Application, Guilin University of Electronic Technology, Guilin 541004, China;
3. Tianjin Key Laboratory Of Optoelectronic Detection Technology and System, School of Electronic and Information Engineering, Tianjin Polytechnic University, Tianjin 300387, China)

Abstract: Eu^{2+}-doped GaN (GaN:Eu^{2+}) nanofibers were synthesized by a facile approach that combined electrospinning and ammonification techniques. SEM and TEM images revealed that the nanofibers consist of GaN nanoparticles with uniform size. XRD result showed that the GaN:Eu^{2+} sample predominantly exhibited the hexagonal phase of GaN (*h*-GaN) and the average grain size was evaluated to be 7.3 nm. Further Raman characterization showed that two extra GaN Raman shifts with the peaks of 252 and 422 cm^{-1} were observed. As was expected, characteristic strong blue emission from Eu^{2+} ions doped in GaN matrix was observed at 407 nm in the photoluminescence spectrum.

Key words: GaN: Eu^{2+} nanofibers, blue emission, electrospinning, ammonification
PACS: 85.60.Dw

电纺丝方法制备 GaN:Eu^{2+} 纳米纤维与发光特性

陈　宇[1,2]，魏学成[1]，刘宏伟[3*]

(1. 中国科学院半导体研究所 集成光电联合国家重点实验室,北京　100083;
2. 桂林电子科技大学 广西精密导航技术与应用重点实验室,广西 桂林　541004;
3. 天津工业大学 天津市光电检测技术与系统重点实验室，天津　300387)

摘要:通过结合静电纺丝和氨化技术方法合成了 Eu^{2+} 掺杂的 GaN(GaN:Eu^{2+})纳米纤维. SEM 和 TEM 图像显示纳米纤维由尺寸均匀分布的 GaN 纳米颗粒组成. XRD 测试结果表明,GaN:Eu^{2+} 样品主要为六方相 GaN(*h*-GaN),其平均粒径为 7.3 nm. 进一步的拉曼测试结果显示出现了两个额外的 GaN 拉曼位移,波数分别位于 252 和 422 cm^{-1}. 室温光致发光谱表明 GaN 基质中的 Eu^{2+} 在 407 nm 处产生了强烈的特征蓝色发光峰.

关　键　词:GaN:Eu^{2+} 纳米纤维;蓝光发射;静电纺丝;氨化技术

中图分类号:TN385　　**文献标识码**:A

Introduction

Since nitride-based light emitting diodes (LEDs) were invented by Nichia Chemical Industries[1], III-V materials, particularly GaN, have drawn much attention. GaN has been considered as one of the most promising materials for constructing optoelectronic devices such as ultraviolet-visible light emitting diodes (LEDs) and laser diodes (LDs), as well as high-temperature and high-power electronic devices, due to their unique properties. Recently, one-dimensional (1D) semiconductor nano-

Received date: 2017-03-24, **revised date**: 2017-09-19　　**收稿日期**:2017-03-24, **修回日期**:2017-09-19

Foundation items:Supported by National Natural Science Foundation of China(11574301, 61274008, 61674147, 11404239), the Opening Project of Guangxi Key Laboratory of Precision Navigation Technology and Application, the National Science Foundation for Post-doctoral Scientists of China (2016M600231), and National Natural Sciences Foundation of Tianjin(14JCQNJC01000)

Biography:CHEN Yu (1975-), male, Beijing, Associate professor, Ph. D. Working on semiconductor materials and devices. E-mail: chenyu@semi.ac.cn

* **Corresponding author**:E-mail: hwliu@foxmail.com

structures have stimulated great interest due to their promising applications in nano-electronic and nano-optoelectronic devices. Thus many devices constructed on 1D GaN-based nanostructures have made great progress[2-4].

Blue light-emitting material is a key block element to the three-primary colour system which can construct a full color display or a white-light emission. Up till now, blue light-emitting material is still a challenge for practical applications due to their high cost and low efficiencies. To solve this problem, rare earths (REs) doped semiconductors have thus been intensively and widely studied in recent years[5-10], because RE elements possess rich energy levels and can emit from infrared to blue light. In view of its band gap, GaN is a promising host material for REs doping. So far, blue emissions from Tm doped GaN[11] and AlGaN[12], as well as GaN based blue LEDs[13] have been successfully realized. However, further more experiments are still need to explore the blue light emission from other RE elements, such as europium (Eu).

Generally, GaN nanowires can be synthesized by the vapor-liquid-solid (VLS) growth mechanism using metal catalyst[14]. Unfortunately, such process will often introduce metal impurities into GaN nanowires, which may restrict their optoelectronic applications. More recently, electrospinning is reported as an emerging technique to fabricate continuous fibers as requiring neither catalysts nor templates[4]. In this paper, the GaN:Eu^{2+} nanofibers were fabricated using electrospinning technique combined with ammonification method. The crystal structure and optical properties of the synthesized nanofibers were mainly studied.

1 Experimental

GaN:Eu^{2+} nanofibers were synthesized by combining electrospinning with ammonification methods. First, 0.5 g $Ga(NO_3)_3$ was solubilized in 1.5 mL deionized water for $Ga(NO_3)_3$ solution, and 0.25 g Polyvinyl pyrrolidone (PVP, Sigma Aldrich, Mw ≈ 1 300 000) was solubilized in 2.5 ml ethanol for PVP solution. After these two kinds of solutions being prepared, 3 g PVP solution was taken to add into $Ga(NO_3)_3$ solution using as precursor, followed by strong magnetic stirring for 2 h. For Eu^{2+} doping, 6 mg $EuBr_2$ (about 1 atm %, Alfa Aesar, 99.99%) powder was added to the obtained precursor solution. Then, the mixture precursor solution was put into an injector for electrospinning[15]. During the electrospinning process, the distance between metal needle tip and collection electrode was 20 cm and the voltage was 13.6 kV. After collected, the samples were sent to a tube furnace for *in situ* ammonification process with an ammonia (NH_3, 99.85%) flow of 20 cm^3/min. The ammonification process was kept for 2 h at 950 ℃. After ammonification, the furnace was cooled down to room temperature under the NH_3 ambience to prevent oxidation.

The crystal structure and morphologies were investigated by X-ray diffraction (XRD, Phlips X'Pert Pro) with Cu Kα (λ = 0.154 056 nm) source, field emission scanning electron microscopy (FE-SEM; Hitachi S-4800) and transmittance electron microscopy (TEM; FEI Tecnai F30). Raman spectrum was carried out on a Jobin-Yvon LabRam HR80 spectrophotometer at room temperature using 532 nm line of a 50 mW diode-pumped solid-state laser as excitation sources. Photoluminescence (PL) spectra was recorded by a spectrophotometer (SHIMADZU RF-540) using 325 nm line of 35mW He-Cd laser (Kimmon) as excitation sources.

2 Results and discussions

Figure 1 shows XRD patterns of undoped GaN and GaN:Eu^{2+} nanofibers ammonificated at 950℃. The undoped GaN and GaN:Eu^{2+} nanofibers predominantly exhibits hexagonal phase of GaN (*h*-GaN) with the most intense three peaks at 2θ = 32.41°, 34.65°, and 36.81° corresponding to (100), (002), and (101) planes of *h*-GaN. Moreover, the other lower peaks can also be attributed to *h*-GaN. The average crystal sizes of the samples can be usually calculated from the intense of (100), (002) and (101) diffraction peaks using the Scherrer formula[16]. Here , the average crystallite sizes of undoped GaN and GaN-Eu^{2+} fibers were estimated to be 25.6 and 7.3 nm, respectively. In addition, it can be found that no diffraction lines of other phases can be observed from XRD spectra. In comparison with GaN nanofibers, the GaN:Eu^{2+} nanofibers exhibit better crystal orientation.

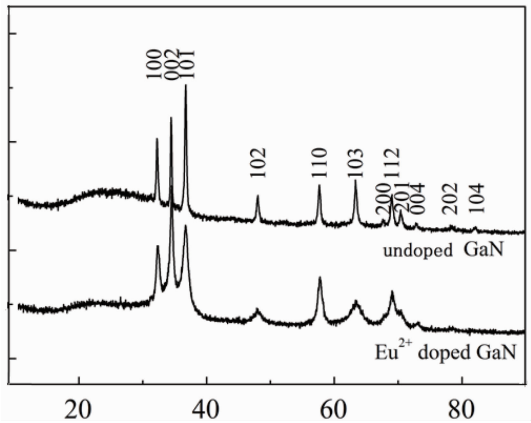

Fig. 1　XRD patterns of undoped GaN nanofibers and GaN:Eu^{2+} (1 at. %) nanofibers ammonification at 950 ℃

图 1　950 ℃氨化 GaN 纳米纤维及 GaN:Eu^{2+} 纳米纤维的 XRD 图谱

In order to further investigate the microstructure and morphologies of the GaN:Eu^{2+} nanofibers, SEM and TEM results are shown in Fig. 2. Figure 2(a) is the SEM image of electrospun nanofibers of $Ga(NO_3)_3$ with PVP. From this image, the diameter of the nanofibers is well-distributed with value of about 100 nm. Figures 2 (b-d) are the SEM and TEM images of the GaN:Eu^{2+} nanofibers after ammonification process. From these images, it can be seen that the nanofibers consist of GaN nanoparticles with uniform size. In particular, the orientation of GaN:Eu^{2+} nanofibers is better than that of GaN nanofibers.

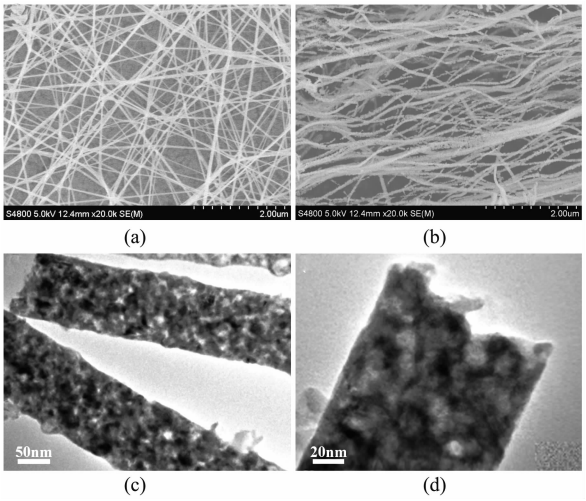

Fig. 2 (a) SEM image of the electrospun nanofibers Ga $(NO_3)_3$ with PVP, (b) SEM image of the GaN:Eu^{2+} nanofibers, (c) and (d) TEM images of the GaN:Eu^{2+} nanofibers

图 2 (a) 静电纺丝法制备的 $Ga(NO_3)_3$ 纳米纤维的 SEM 图,(b) GaN:Eu^{2+} 纳米纤维 SEM 图,(c) 和(d) GaN:Eu^{2+} 纳米纤维 TEM 图

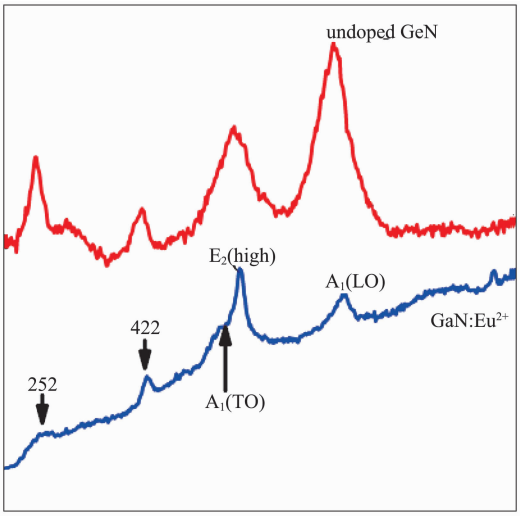

Fig. 3 Raman spectra of the undoped GaN nanofibers and GaN:Eu^{2+} nanofibers prepared at 950 ℃ which excited by a 532 nm laser

图 3 GaN 纳米纤维及 GaN:Eu^{2+} 纳米纤维拉曼光谱

As shown in Fig. 3, both the undoped GaN nanofibers and GaN:Eu^{2+} nanofibers present the predominant two Raman shifts which located at 535 and 567 cm^{-1} on a broad background, and these two peaks can be assigned to A_1(TO) and E_2(high) of *h*-GaN, respectively. The E_2(high) peak indicates that the structure of the nanofibers is hexagonal crystal phase[17]. Furthermore, the peak at 733 cm^{-1} can be assigned to the A_1(LO) mode, which suggests that the carrier concentration of the nanofibers is low[18]. Such results are well in accord with the analysis derived from the XRD data. Additionally, the appearances of both 252 and 422 cm^{-1} peaks are confined by the space group in first-order Raman scattering. The Raman shift at 252 cm^{-1} stems from surface disorders or finite-size effects[19], and the Raman shift of 422 cm^{-1} results from the vibration of N-rich octahedral Ga-N_6 bonds[20].

Figure 4 presents PL spectra of the undoped GaN nanofibers and GaN:Eu^{2+} nanofibers excited by a He-Cd laser using 325 nm at room temperature. In contrast with the undoped GaN PL spectrum, besides a very weak emission peak of matrix material of GaN band edge emission, a strong violet-blue emission range from 380 nm to 490 nm can be observed from the GaN:Eu^{2+} nanofibers with the center at 407.0 nm. Such emission band could be assigned to transition between levels $4f^6 5d^1$ and $4f$. It is well known that, the transition in Eu^{3+}-doped matrix system is electron jumping from level $5d^0$ to levels $4f$. Eu^{3+}-based PL peaks often appear in between 580 nm and 650 nm. In the PL spectrum, GaN:Eu^{2+} nanofibers do not show any feature emission of Eu^{3+} ions. According to Refs. [10-11], the energy which excites the RE ions is mainly achieved from the direct band-gap absorption of GaN host matrix. After absorbed by the host matrix, the energy can be transferred to RE ions. Thus RE ions can also absorb energy and bound to high levels which result in radiative transition. Because the electronegativities of Ga and RE atoms are different, the RE ions could lead into charge traps and then can attract an electron or a hole. Furthermore, the trap could capture an opposite charge and form a bound exciton. The excitons recombine transfer energy to intra-$4f$ electron of RE^{3+} i-

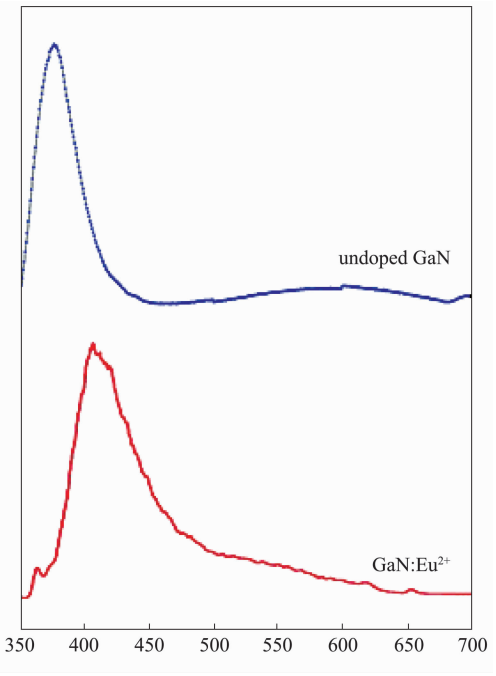

Fig. 4 PL spectra of the undoped GaN nanofibers and GaN:Eu^{2+} nanofibers which excited by a 325 nm He-Cd laser at room temperature

图 4 325 nm He-Cd 激光激发的 GaN 及 GaN:Eu^{2+} 纳米纤维的室温光致发光谱

ons and excite them to high levels to generate radiative transition[21]. Besides, a broad green-yellow emission band (G-band) in visible light region can also be observed in Fig. 4. According to Nyk *et al*[22], the G-band is due to the lattice defects.

3 Conclusions

In summary, GaN:Eu^{2+} nanofibers have been prepared using electrospinning combined with ammonification methods. XRD results showed that the nanofibers were of hexagonal phase of GaN. Both SEM and TEM images revealed the nanofibers consisting of GaN nanoparticles with uniform size. In our results, two extra GaN Raman shifts were observed with the peaks of 252 and 422 cm^{-1}, which are confined in first-order Raman scattering and are attributed to phonon activated by surface disorders or finite-size effects and vibration mode of octahedral Ga-N_6 bonds, respectively. From PL spectra, the blue characteristic peak of Eu^{2+} ion was observed. This suggests that GaN nanofibers are proper host material for REs doping and could be integrated with modern optoelectronics.

Acknowledgments

This work was supported by National Natural Science Foundation of China under Grant 11574301, 61274008, 61674147 and 11404239, by the Opening Project of Guangxi Key Laboratory of Precision Navigation Technology and Application, by the National Science Foundation for Post-doctoral Scientists of China (Nos. 2016M600231), and by the National Natural Science Foundation of Tianjin under Grant 14JCQNJC01000.

References

[1] Nakamura S, Mukai T, Senoh M. Candela-class high-brightness InGaN/AlGaN double-heterostructure blue-light-emitting diodes[J]. *Appl. Phys. Lett.* 1994, **64**: 1687 -9.

[2] Johnson J C, Choi H J, Knutsen K P, *et al*. Single gallium nitride nanowire lasers[J]. *Nat. Mater.* 2002, **1**: 106 -110.

[3] Zhong Z, Wang D, Cui Y, et al. Nanowire crossbar arrays as address decoders for integrated nanosystems[J]. *Science*, 2003, **302**: 1377 -9.

[4] Wu H, Sun Y, Lin D D, *et al*. GaN nanofibers based on electrospinning: facile synthesis, controlled assembly, precise doping, and application as high performance UV photodetector[J]. *Adv. Mater.* 2009, **21**: 227 -31.

[5] Steckl A J, Zavada J M. Optoelectronic properties and applications of rare-earth-doped GaN[J]. *MRS Bull.* 1999, **24**: 33 -8.

[6] Kim J H, Holloway P H. Room-temperature photoluminescence and electroluminescence properties of sputter-grown gallium nitride doped with europium[J]. *J. Appl. Phys.* 2004, **95**:4787 -90.

[7] Pan X J, Zhang Z X, Jia L, *et al*. Room temperature visible green luminescence from a-GaN:Er film deposited by DC magnetron sputtering [J], *J. Alloys Compd*, 2008, **458**: 579 -82.

[8] Wang R, Steckl A J. Effect of growth conditionson Eu3 + luminescence in GaN. [J]. *Cryst. Growth*. 2010, **312**: 680 -4.

[9] Gautam A, van Veggel Frank C J M. Blue electroluminescence from Eu^{2+}-doped GaN@ SiO_2 nanostructures tuned to industrial standards [J]. *Chem. Mater.* 2011, **23**: 4817 -23.

[10] Pan X J, An X Y, Zhang Z X, *et al*. Structural and optical properties of GaN:Eu nanoparticles synthesized by simple ammonification method [J]. *J. Alloy. Comp.* 2012, **519**: 67 -71.

[11] Wang Y Q, Steckl A J. Three-color integration on rare-earth-doped GaN electroluminescent thin films[J]. *Appl. Phys. Lett.* 2003, **82**: 502 -4.

[12] Lee D S, Steckl A J. Enhanced blue emission from Tm-doped AlGaN electroluminescent thin films[J]. *Appl. Phys. Lett.* 2003, **83**: 2094 -6.

[13] Yang K Y, Oh S C, Cho J Y, *et al*. Direct indium tin oxide nanoparticle printing technique for improvement of light extraction efficiency of GaN-based LEDs[J]. *J. Electrochem. Soc.* 2010, **157**: H1067 -70.

[14] Chen X, Xu J, Wang R M, *et al*. High-quality ultra-fine GaN nanowires synthesized via chemical vapor deposition[J]. *Adv. Mater.* 2003, **15**: 419 -21.

[15] Zhou J Y, Zhou M, Chen Z Y, *et al*. SiC nanotubes arrays fabricated by sputtering using electrospun PVP nanofiber as templates[J]. *Surf. Coat. Tech.* 2009, **203**:3219 -23.

[16] Scherrer P. Gottinger Nachrichten Gesell, ft/fmax > 150/210 GHz AlGaN/GaN HFETs with regrown n-GaN Ohmic contacts by MOCVD [J]. *Infrared Millim Waves*. 2016, **5**:534 -537.

[17] Ortony J W, Foxonz C T. Group III nitride semiconductors for short wavelength light-emitting devices[J]. *Rep. Prog. Phys.* 1998, **61**: 1 -75.

[18] Gebicki W, Adamowicz L, Strzeszewski J, *et al*. Raman scattering study of gallium nitride heavily doped with manganese[J]. *Mater. Sci. Eng. B.* 2001, **82**:182 -4.

[19] Pan G Q, Kordesch M E, Van Patten P G. Room-temperature synthesis of GaN nanopowder[J]. *Chem. Mater.* 2006, **18**: 5392 -4.

[20] Ning J Q, Xu S J, Yu D P, *et al*. Raman scattering from gallium nitride nanowires: Is it a vibration mode of N-rich Ga - N bond configuration[J]. *Appl. Phys. Lett.* 2007, 91: 103117(1 -3).

[21] Lozykowski H J. Kinetics of luminescence of isoelectronic rare-earth ions in III-V semiconductors [J]. *Phys. Rev. B* 1993, 48:17758 -69.

[22] Nyk M, Jabłonski J M, Strezk W, *et al*. Yellow emission of GaN nanocrystals embedded in a silica xerogel matrix [J]. *Opt. Mater.* 2004, **26**: 133 -6.