Fabrication and optical properties of InGaN/GaN multiple quantum well light emitting diodes with amorphous $BaTiO_3$ ferroelectric film*

Peng Jing(彭 静)[a)b)†], Wu Chuan-Ju(吴传菊)[b)], Sun Tang-You(孙堂友)[c)], Zhao Wen-Ning(赵文宁)[c)], Wu Xiao-Feng(吴小锋)[c)], Liu Wen(刘 文)[c)], Wang Shuang-Bao(王双保)[c)], Jie Quan-Lin(揭泉林)[a)], and Xu Zhi-Mou(徐智谋)[c)]

[a)] *Department of Physics, Wuhan University, Wuhan* 430072, *China*

[b)] *College of Sciences, Wuhan University of Science and Technology, Wuhan* 430081, *China*

[c)] *Wuhan National Laboratory for Optoelectronics & College of Optoelectronic Science and Engineering, Huazhong University of Science and Technology, Wuhan* 430074, *China*

(Received 8 December 2011; revised manuscript received 5 February 2012)

$BaTiO_3$ (BTO) ferroelectric thin films are prepared by the sol–gel method. The fabrication and the optical properties of an InGaN/GaN multiple quantum well light emitting diode (LED) with amorphous BTO ferroelectric thin film are studied. The photoluminescence (PL) of the BTO ferroelectric film is attributed to the structure. The ferroelectric film which annealed at 673 K for 8 h has the better PL property. The peak width is about 30 nm from 580 nm to 610 nm, towards the yellow region. The mixed electroluminescence (EL) spectrum of InGaN/GaN multiple quantum well LED with 150-nm thick amorphous BTO ferroelectric thin film displays the blue–white light. The Commission Internationale De L'Eclairage (CIE) coordinate of EL is (0.2139, 0.1627). EL wavelength and intensity depends on the composition, microstructure and thickness of the ferroelectric thin film. The transmittance of amorphous BTO thin film is about 93% at a wavelength of 450 nm–470 nm. This means the amorphous ferroelectric thin films can output more blue-ray and emission lights. In addition, the amorphous ferroelectric thin films can be directly fabricated without a binder and used at higher temperatures (200 °C–400 °C). It is very favourable to simplify the preparation process and reduce the heat dissipation requirements of an LED. This provides a new way to study LEDs.

Keywords: InGaN/GaN multiple quantum well light emitting diodes, ferroelectric film, $BaTiO_3$, optical properties

PACS: 77.84.–s, 78.20.–e, 81.16.Be **DOI:** 10.1088/1674-1056/21/6/067702

1. Introduction

Recently, much attention has been paid to ferroelectric thin films in integrated optoelectronic device applications as they have prominent properties such as large electro–optic coefficients and relatively low optical losses.[1−3] Our group investigated the microstructure and optical properties of amorphous $Ba_{0.7}Sr_{0.3}TiO_3$ (BST0.7) ferroelectric thin films deposited on a silicon substrate.[4,5] We demonstrated the successful operation of a monolithically integrated Mach–Zehnder interferometer (MZI) optical modulator based on metal organic solution-derived polycrystalline BST0.7 thin films deposited at a relatively low temperature of 550 °C.[6] Other researchers[7−9] reported on the intense photoluminescence (PL) emissions from amorphous ABO_3-type perovskites such as $BaTiO_3$ (BTO), $CaTiO_3$ (CTO), $PbTiO_3$ (PTO), $SrTiO_3$ (STO), and relevant materials such as (Ba,Sr)TiO_3 (BST) and Pb(Zr,Ti)O_3 (PZT) in powder samples or thin solid films. In the present paper, the fabrication and optical properties of an InGaN/GaN multiple quantum well (MQW) light emitting diode (LED) with amorphous BTO ferroelectric film are studied in detail.

*Project supported by the National Natural Science Foundation of China (Grant Nos. 61076042 and 60607006), the Special Project on Development of National Key Scientific Instruments and Equipment of China (Grant No. 2011YQ16000205), and the National High Technology Research and Development Program of China (Grant No. 2011AA03A106).

†Corresponding author. E-mail: jingmathfly@yahoo.com.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

2. Experiment

2.1. Fabrication of LED chip

The InGaN/GaN MQW LED structure was grown by metal–organic chemical vapour deposition (MOCVD) on (0001)-sapphire.[10−12] The structure is shown in Fig. 1. First, the GaN buffer layer (about 30 nm) was deposited on the sapphire at a lower temperature. Then the sapphire was heated up to 1040 °C and SiO_2 dopping n-GaN (4 μm) was grown on the sapphire. The n-AlGaN (about 50 nm) was deposited at 900 °C. And, a number of 5 InGaN(1.8 nm)/GaN(11 nm) multiple quantum wells were grown as an active region at a temperature between 700 °C and 740 °C. The interface of every layer of MQW was extremely smooth. On the MQW layers, p-AlGaN (50 nm) was grown at 900 °C. After the epitaxial wafer was grown and annealed, LED mesa structures were obtained by standard photolithographic patterning followed by inductively coupled plasma (ICP) etching to expose the n-type cladding layer. Ni/Au and Ni/A1 were deposited as Ohmic contacts to p-type GaN and n-type GaN respectively.

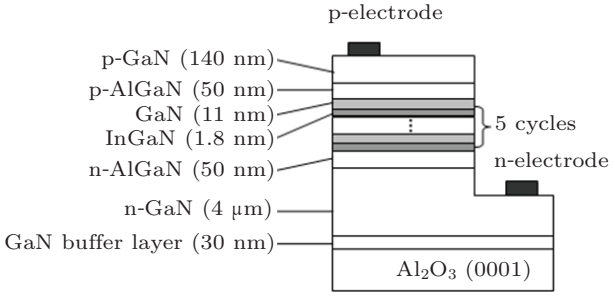


Fig. 1. Structure of the MQW LED.

2.2. Fabrication of amorphous BTO ferroelectric film

BTO ferroelectric films were prepared by the sol–gel method. First, 1 molar barium acetate was accurately weighed with an analysis balance and added into 25-ml glacial acetic acid. The solution was stirred until the barium acetate was completely dissolved. Then 1 molar acetylacetone was added into the solution as a stabilizer. The tetrabutyl titanate was weighted accurately according to a molar ratio of 1:1 between barium acetate and tetrabutyl titanate and was added into the synthesized solution. Finally, an amount of glacial acetic acid was added to dilute the solution to obtain the stable and clear BTO colloidal solution.

We used monocrystalline silicon (111) and fused quartz as substrates in the deposition experiments. The BTO colloidal solution was dripped on the polished substrates. A series of stable BTO ferroelectric films was obtained after they had been annealed at different temperatures.

2.3. Analyses of BTO ferroelectric film microstructure and optical properties

The microstructure of the BTO thin film was analyzed by X-ray diffraction (XRD, Rigaku RINT2100) with a copper target, at 40 kV and 40 mA. Surface morphology of the film was observed using an atomic force microscopy (AFM, Seiko SPA300) and field emission scanning electronic microscopy (FESEM, Hitachi S-4700). The thickness of thin film was measured by a Nanometrics (Nanospec/AFT 5000) machine and determined by an SEM photograph of cross sections of the sample. The transmittance of amorphous BST0.7 thin film on fused quartz has been studied using a double beam ultraviolet-visible (UV-VIS-NIR) spectrophotometer (JASCO, V-570DS) in a wavelength range of 190 nm–900 nm. The PL spectrum of the film was measured by the fluorescence spectrometer (IASCO, FP-6500).

2.4. Fabrication and analyses of optical properties of LED chips with amorphous BTO ferroelectric film

The fabrication technology is as follows.

(i) The insulating cement at a moderate dose was dripped in the circle on the Al bottom. Because the blue LED chip is made of a sapphire insulating substrate, we use the insulating cement to fix the chip.

(ii) The chip was pasted under microscope and was kept smooth as much as possible.

(iii) The fixed chip was baked at 150 °C for 2 h to solidify the glue.

(iv) The wires were drawn with a wire drawing machine as electrode leads.

(v) The BTO thin films were spin-coated on the fixed chips.

(vi) The film was annealed at different temperatures to obtain the amorphous thin films with PL emission properties.

The finished single chip was 1 mm×1 mm in size. The chip was placed on the probe station for the

electroluminescence (EL) test. The injection current range was 0–150 mA.

3. Results and discussion

3.1. Microstructure and surface morphology

XRD patterns of the BTO film samples annealed for 8 h at different temperatures are shown in Fig. 2. There appears to be no clear sharp diffraction peak in the films annealed at 473 K and 673 K. However, several peaks are observed at 22.3°, 31.7°, 39.1°, 45.5°, 51.2°, and 56.5° in the sample annealed at 873 K. The (110) peak at $2\theta = 31.7°$ is especially sharp. It is believed that BTO ferroelectric films are in an amorphous phase when they are annealed at 473 K and 673 K, but a crystalline phase occurs when they are annealed at 873 K. The higher the temperature, the more crystalline the BTO film is. These films are preferentially grown in (100) orientation.

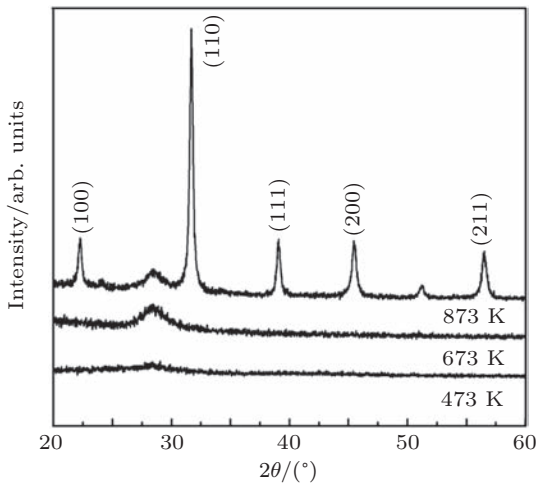


Fig. 2. XRD patterns of BTO ferroelectric films annealed for 8 h at 473 K, 673 K, and 873 K.

Figure 3 shows the AFM images of BTO ferroelectric films for (a) the amorphous phase annealed at 473 K and (b) the crystalline phase annealed at 873 K. Typical protuberant island structures can be seen on the surface of the two films, without cracks and voids. The surface protrusion size of the amorphous film is about 20 nm and the root mean square (RMS) roughness of the film surface is 1.8 nm per 1 μm^2 evaluated from AFM image (a). The crystalline film surface is rougher, the protrusion size is about 50 nm, and the RMS roughness is 17.6 nm per 1 μm^2. For optical films, RMS roughness is one of the most important parameters that influence optical transmission. A RMS roughness less than 1 nm might be more suitable for applications.

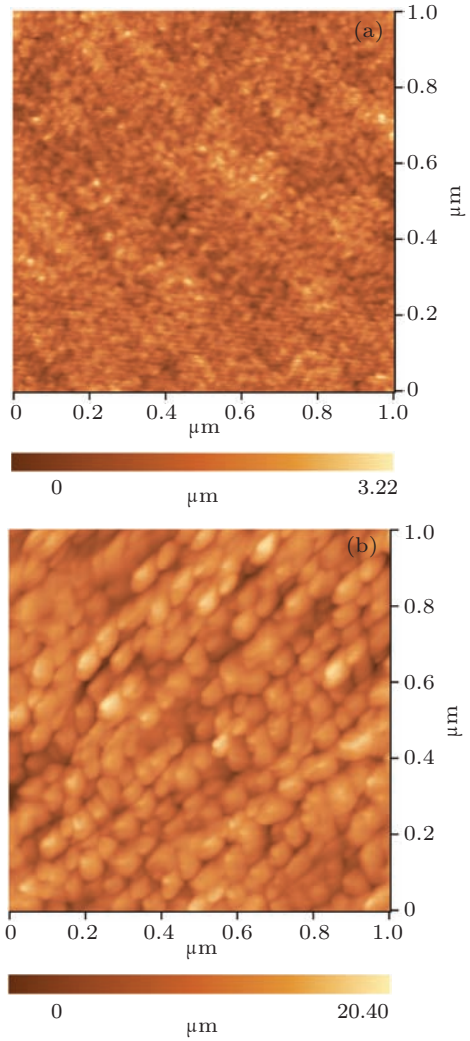


Fig. 3. (colour online) AFM images of (a) amorphous and (b) crystalline BTO ferroelectric films.

3.2. Optical properties

3.2.1. Optical transmittance of amorphous BTO thin films

The optical transmittance spectrum of amorphous BTO thin film on fused quartz substrate has been recorded in a wavelength range of 190 nm–900 nm as shown in Fig. 4. Roughly, the spectrum can be divided into two regions: a transparent oscillating region, and a zone of strong absorption, where the transmittance decreases drastically. The transmittance of an amorphous BTO thin film is about 93% at a wavelength of 450 nm–470 nm and it is the same as that of the fused quartz.

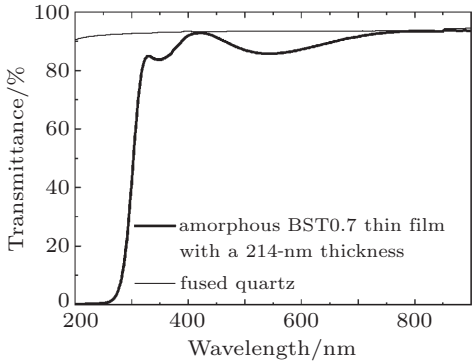


Fig. 4. Transmittance spectra of fused quartz and an amorphous BTO thin film on a fused quartz substrate with about 150-nm in thickness.

3.2.2. PL spectra of amorphous BTO thin films

Figure 5 shows the PL spectra of the BTO ferroelectric films annealed for 8 h at different temperatures: curve *a* 473 K, curve *b* 673 K, and curve *c* 873 K, excited by a 450-nm line. All the data were tested at room temperature. Intense PL spectra in BTO ferroelectric films were observed when they were annealed at 473 K and 673 K for 8 h. The emission wavelengths range from 540 nm to 660 nm in the visible region. The PL properties were affected by the heat treatment technology. This is mainly related to the microstructures of the BTO thin films. The peak width of the PL spectrum of the sample annealed at 473 K is about 20 nm, spanning from 610 nm to 630 nm. It shifts towards the long wavelength region. For the sample annealed at 673 K, the peak width is about 30 nm, spanning from 580 nm to 610 nm. It shifts towards the yellow region. The intensity of the latter is higher than that of the former. Curve *c* in Fig. 5 seems to be a straight line with a value of zero which indicates that film annealed at 873 K has no PL properties. Figure 2 shows that BTO ferroelectric films annealed at 473 K and 673 K are amorphous, but are crystalline when annealed at 873 K. So the amorphous BTO ferroelectric film has PL in the visual region and the crystalline BTO ferroelectric films annealed at 873 K become featureless. The PL of the BTO ferroelectric film is attributed to the difference between two kinds of structures.[13] Figure 6 shows the structures of (a) crystalline and (b) amorphous BTO films. Figure 6(b) shows TiO_6 octahedron and TiO_5 pyramid structures. The transformation takes place between TiO_6 and TiO_5 when the film is irradiated by light. Electrons escape from the O-$2p^6$ band to the Ti-$3d^2$ band. But the energy level of Ti-$4s^2$ is a little lower than Ti-$3d^2$, so the electrons continue going to Ti-$4s^2$. The electrons combine with holes in the band and excite the photons. The process can be demonstrated by the following formulas:

$$O(2p^6) - e \rightarrow O(2p^5), \quad (1)$$

$$Ti(3d^2) + e \rightarrow Ti(4s^2), \quad (2)$$

$$O(2p^6) + Ti(3d^2) \rightarrow O(2p^5) + Ti(4s^2). \quad (3)$$

When the crystallization in Fig. 6(a) is reached, only the TiO_6 cluster exists and the PL vanishes, showing that a complete order is not suitable for a good PL emission. The PL intensity depends on the integrity of amorphous microstructures. So the property of sample annealed at 673 K is better than that annealed at 473 K. It is expected that the optimum annealed temperature is the temperature corresponding to the best PL intensity.

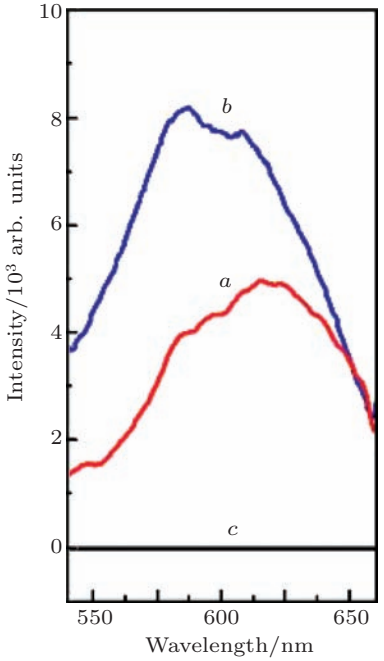


Fig. 5. (colour online) PL spectra of BTO ferroelectric films annealed for 8 h at different temperatures: curve *a* 473 K, curve *b* 673 K, and curve *c* 873 K.

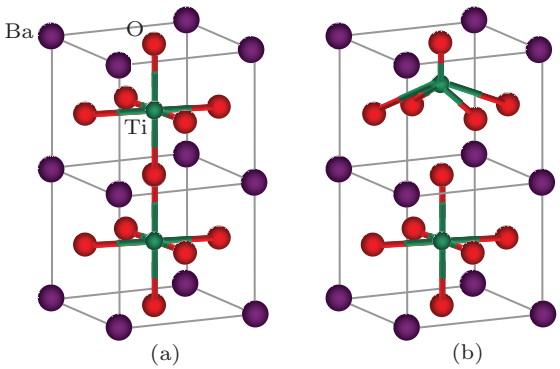


Fig. 6. (colour online) Structures of (a) crystalline, (b) amorphous BTO ferroelectric films.

Figure 7 shows the PL spectra of BTO ferroelectric films with different excitation wavelengths: curve *a* 450 nm, curve *b* 455 nm, curve *c* 460 nm, and curve *d* 465 nm. The emission regions, peak wavelengths and widths scarcely change when the excitation wavelength has a variation of 5 nm, spanning from 450 nm to 465 nm, but the intensity decreases with the increase of excitation wavelength.

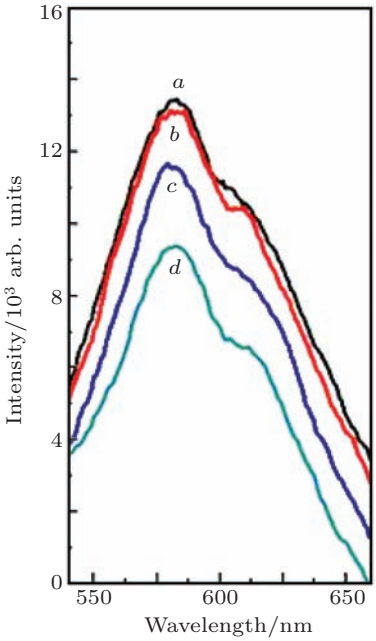


Fig. 7. (colour online) PL spectra of amorphous BTO films excited at wavelengths: curve *a* 450 nm, curve *b* 455 nm, curve *c* 460 nm, and curve *d* 465 nm.

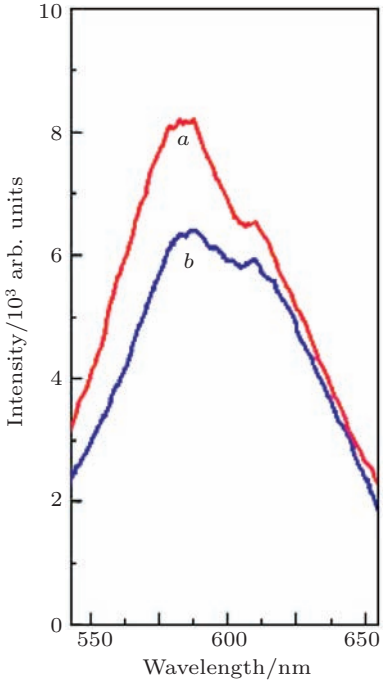


Fig. 8. (colour online) PL spectra of amorphous BTO films with thickness values of curve *a* 100 nm and curve *b* 150 nm.

Figure 8 shows the PL spectra of BTO ferroelectric films with different thicknesses: curve *a* is 100 nm and curve *b* is 150 nm. The emission regions, peak wavelengths, and widths also scarcely change when the thickness of BT ferroelectric film changes from 100 nm to 150 nm, but the intensity is enhanced. This is mainly due to the increase of the total intensity of light-emitting materials in a certain thickness range.

3.2.3. EL spectrum of LED chip with amorphous BTO ferroelectric film

The EL spectra of the LED chip in different injection currents were measured. The LED chip emits high-brightness and a very pure blue light at an injection current of 120 mA as shown in Fig. 9. The dominant wavelength is 460.06 nm. The EL spectrum is very narrow and the FWHM is only 18.9 nm.

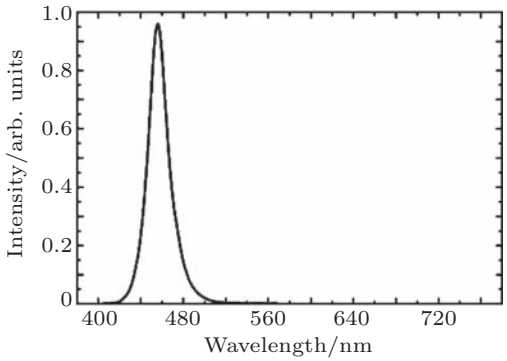


Fig. 9. EL spectrum of the LED chip at an injection current of 120 mA.

Figure 10 shows the EL spectrum of the LED chip with a 150-nm thick amorphous BTO film at an injection current of 120 mA. It is obvious that the EL peak wavelengths include blue and yellow light. Because the intensity of blue light is much stronger than that of yellow light, the mixed EL displays the blue–white light.

Figure 11 shows the photos of the bare chip (a) and the EL sample (b). The CIE coordinate of EL is (0.2139, 0.1627). The colour is close to the white area, but there is a certain distance from the standard pure white light colour coordinates of (0.33, 0.33). The EL intensity of the ferroelectric thin film can be improved by being doped with RE or metal elements.[8] Additionally, increasing the thin film thickness and optimizing the heat treatment technology is also conducive to the improvement of EL intensity and quality.

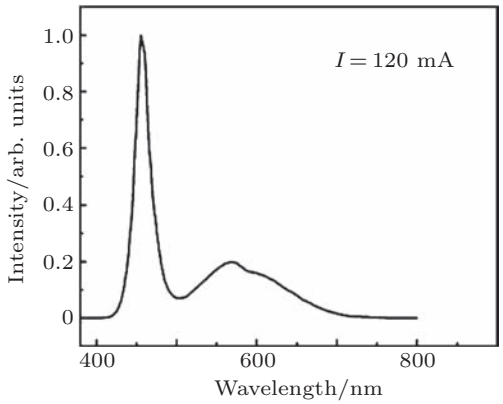


Fig. 10. EL spectrum of the LED chip with a 150-nm thick amorphous BTO film at an injection current of 120 mA.

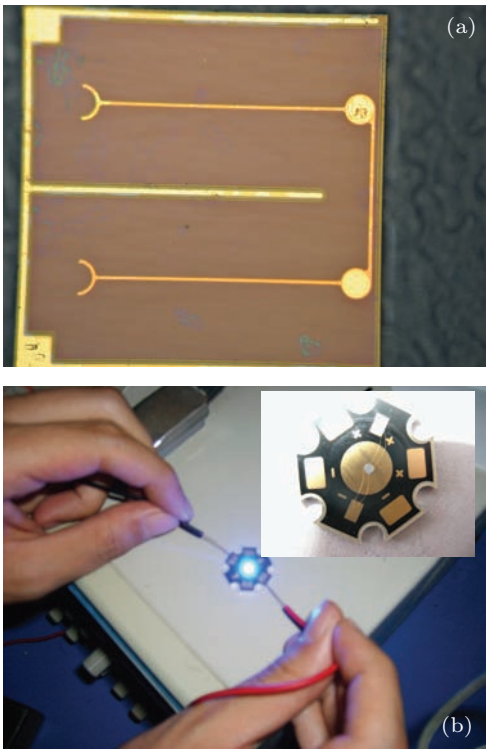


Fig. 11. (colour online) Photos of the bare chip (a) and the EL sample (b).

4. Summary

The exploratory experiments of a white light LED chip based on amorphous ferroelectric thin films have been accomplished in this paper. EL wavelength and intensity depend on the composition and microstructure of ferroelectric thin film. EL properties of ferroelectric thin film can be easily be modulated through the selective control of ferroelectric thin film composition and microstructure. So it is very convenient for controlling the optical parameters of the white LED. Another advantage of the amorphous ferroelectric thin film applied in a white LED is a high degree of light transmission in the visible region. It shows a high optical transmittance in the visible wavelength range of 380 nm–780 nm. The transmittance of the amorphous BTO thin film is about 93% at a wavelength range of 450 nm–470 nm and is the same as that of the fused quartz. The transmittance of the commercial YAG:Ce phosphor is about 80% in the blue band.[14] It is obvious that the amorphous ferroelectric thin film can output more blue light and emission light than the YAG:Ce phosphor because of its high transmittance in the visible light wavelength. In addition, the amorphous ferroelectric thin film can be directly fabricated without a binder and used at a higher temperature (200 °C–400 °C). It is very favourable to simplify the preparation process and reduce the heat dissipation requirement for an LED. This provides a new way to study LEDs.

References

[1] Jiang P, Si D W, Zhu H W, Li P G, Wang S L, Cui C and Tang W H 2011 *Acta Phys. Sin.* **60** 117203 (in Chinese)
[2] Kim D Y, Moon S E, Kim E K, Lee S J, Choi J J and Kim H E 2003 *Appl. Phys. Lett.* **82** 1455
[3] Samantaray C B, Sim H and Hwang H 2004 *Physica* B: *Conden. Matter* **351** 158
[4] Xu Z M, Tanushi Y, Suzuki M, Wakushima K and Yokoyama S 2006 *Thin Solid Films* **515** 2326
[5] Xu Z M, Suzuki M, Tanushi Y and Yokoyama S 2006 *Jpn. J. Appl. Phys.* **45** 3482
[6] Xu Z M, Tanushi Y, Suzuki M and Yokoyama S 2006 *Appl. Phys. Lett.* **88** 161107
[7] Pontes F M, Longo E, Leite E R, Lee E J H, Varela J A, Pizani P S, Campos C E M, Lanciotti F, Mastellaro V and Pinheiro C D 2002 *Mater. Chem. Phys.* **77** 598
[8] Melo D M A, Cesar A, Martinelli A E, Silva Z R, Leite E R, Longo E and Pizanni P S 2004 *J. Solid State Chem.* **177** 670
[9] Pizani P S, Leite E R, Pontes F M, Paris E C, Rangel J H, Lee E J H, Longo E, Delega P and Varela J A 2000 *Appl. Phys. Lett.* **77** 824
[10] Zhu L H, Cai J F, Li X Y, Deng B and Liu B L 2010 *Acta Phys. Sin.* **59** 4996 (in Chinese)
[11] Xing Y H, Deng J, Han J, Li J J and Shen G D 2009 *Acta Phys. Sin.* **58** 590 (in Chinese)
[12] Li W J, Zhang B, Xu W L and Lu W 2009 *Acta Phys. Sin.* **58** 3421 (in Chinese)
[13] Orhan E and Varela J A 2005 *Phys. Rew.* B **71** 085113
[14] Nishiura S, Tanabe S, Fujioka K and Fujimoto Y 2011 *Opt. Mater.* **33** 688