InGaN-based 405 nm near-ultraviolet light emitting diodes on pillar patterned sapphire substrates

Pekka T. Törmä,*[a] Muhammad Ali,[a] Olli Svensk,[a] Sami Suihkonen,[a] Markku Sopanen,[a] Harri Lipsanen,[a] Mikael Mulot,[b] Maxim A. Odnoblyudov[c] and Vladislav E. Bougrov[c]

Received 26th January 2010, Accepted 21st April 2010
DOI: 10.1039/c001607a

A study of GaN films and nitride based light emitting diodes (LEDs) grown on low density pillar structure (LDPS) and high density pillar structure (honeycomb like) sapphires patterned by chemical wet etching is described. Both types of patterned sapphire substrate (PSS) offered reduced defect density and improved performance of near-ultraviolet LED. In the case of LDPS patterned sapphire the correct choice of the pillar depth was found to be crucial for high quality crystal growth. A reduction of threading dislocation (TD) density from the level of 10^8 cm^{-2} down to the level of 2 × 10^9 cm^{-2} was observed. It was found that mostly enhanced light extraction rather than improved material quality caused the improvement of the LED performance.

Introduction

A white light emitting diode (LED) using an InGaN-based ultraviolet (UV)-LED as a pumping source is the most promising solid-state source for illumination. InGaN-based LEDs are also used in various applications *e.g.*, traffic signals, large displays *etc.*[1] Therefore, there is an enormous demand for more efficient LEDs. The high threading dislocation (TD) densities in the range of 10^9 to 10^{10} cm^{-2} caused by the lattice mismatched substrates like sapphire, SiC, and Si limits the internal quantum efficiency (IQE) of GaN-based devices[2] although they can have exceptional high performance regardless of the high density of TDs.[3] Approaches such as epitaxial lateral overgrowth (ELOG),[4] pendeo epitaxy (PE),[5] multistep method (MSM),[6] patterned sapphire substrates (PSSs),[7] and their combinations[8] have been introduced for reducing the TD density. A drawback of ELOG and PE is a need to perform epitaxial growth twice. While the MSM and PSSs have an advantage of a single epitaxial process.

Recently there has been activity related to growth of GaN and LED structures on PSSs. The mechanically and chemically strong nature of sapphire makes patterning a challenging task. There are three methods to solve this: inductive coupled plasma reactive ion etching (ICP-RIE),[9,10] high temperature wet etching[11–13] or laser-induced wet etching.[14] The main difference between these methods is the anisotropic and isotropic natures of ICP-RIE and wet etching, respectively. For this reason wet etched patterns on sapphire have mainly been holes on the surface.[15] With plasma methods a wider range of patterns such as stripes,[7,10,15,16] holes[8] and pillars[17] have been used as the sapphire substrate surface patterns in the epitaxial growth of GaN-based materials. Many groups have reported improved GaN material quality and LED performance when the epitaxial structure has been grown on PSS. In principle the improved performance is claimed to be caused by two factors, enhanced light extraction efficiency (LEE) by PSS and improved IQE due to the decrease of TD density. However, there have been opposite opinions on how important a factor the reduced TD density is for the performance of LEDs grown on PSSs.[8,13,16,17]

In this paper we present a study of high quality epitaxial GaN films and LED structures grown directly on several types of wet etched pillars on sapphire. GaN films having a TD density in the range of 2–10 × 10^8 cm^{-2} were fabricated. Two main aspects were found when the LEDs were grown on these substrates. The photoluminescence (PL) mostly depended on the pattern type and depth but did not really correlate with the TD density. The electrical properties of the LEDs strongly depended on the choice of correct pattern type on the sapphire. Details of the material quality, optical end electrical properties of the near UV 405 nm LED structures on conventional sapphire (CS) and pillar PSSs are presented.

Experimental

C-plane sapphire substrates used in this study were patterned with a high temperature wet etching acid mixture of H_2SO_4–H_3PO_4 at 300 °C. A SiO_2 film served as an etching mask and it was patterned using standard photolithography. A thin SiO_2 film on the back side was used to avoid unwanted etching of the back side of the substrate. Two different mask patterns were used for patterning. A low density pillar structure (LDPS) and a high density pillar structure (honeycomb) consisted of hexagonal pillars having 4 μm diameter with 3 μm spacing and 3 μm diameter with 1.5 μm spacing, respectively. Fig. 1(a) and (b) show scanning electron microscopy (SEM) images of both LDPS and honeycomb pillars etched on sapphire, respectively. Three different pillar depths of 300, 550 and 700 nm for LDPS and 500, 800 and 1300 nm for honeycomb pillars were fabricated.

The GaN films and LED structures studied in this work were grown in a vertical flow 3 × 2″ close-coupled showerhead (CCS) MOVPE reactor. Ammonia was used as a nitrogen precursor. For elements of group III trimethylgallium (TMGa) and trimethylindium (TMI) were used as precursors for gallium and

[a]*Department of Micro and Nanosciences,Micronova, AaltoUniversity, 02150 Espoo, Finland. E-mail: pekka.torma@tkk.fi; Fax: +358 9 470 25008; Tel: +358 9 470 23121*
[b]*OptoGaN GmbH, Konrad Adenauer Allee 11, 44263 Dortmund, Germany*
[c]*OptoGaN Oy, Tietotie 3, 02150 Espoo, Finland*

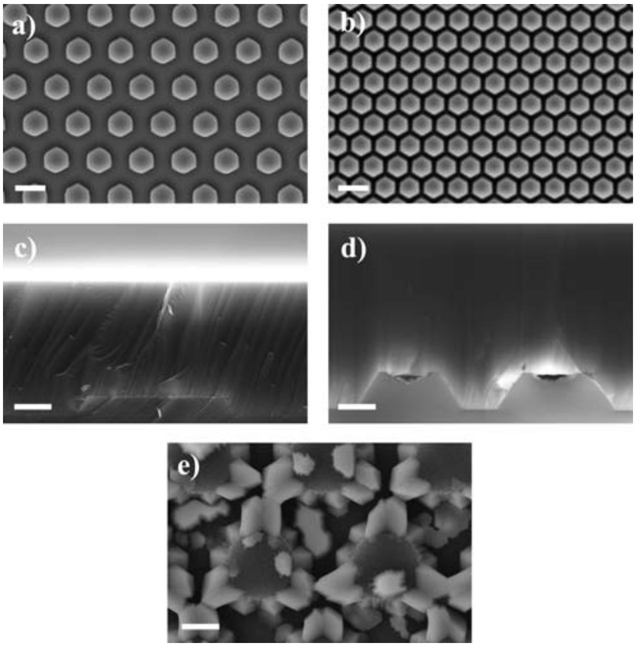

Fig. 1 SEM images of the (a) LDPS and (b) honeycomb PSSs. In (c) and (d) the cross section SEM images of the GaN films grown on LDPS substrate with 300 nm pillar height and on honeycomb substrate with 1050 nm pillar height. The small holes on top of pillars in (d) are caused by the interference effect under the mask during the light exposure in the lithography process. These kind of small holes were present in some of the pillars patterned with the high density mask. Image (e) shows why the higher pillar depth with LDPS substrates than 700 nm was not used in this study. With higher pillar depth (over 1000 nm in (e)) the fast growing horizontal GaN rods originating from the crossroads of the sapphire crystal planes became a significant problem with LDPS substrates. The scale bars correspond to 5 μm in (a) and (b), to 1 μm in (c) and (d), and to 2μm in (e).

indium, respectively. The dopants of the n- and p-type layers were silane and bis-cyclopentadienyl magnesium (Cp_2Mg), respectively. Both GaN films and LED structures were investigated with both of the PSS types and with reference samples on CS. The GaN films were grown by the following procedure. A low-temperature nucleation layer and a 2.5 μm thick undoped GaN buffer grown at elevated temperature were followed by 2 μm thick undoped GaN grown at standard GaN growth temperature. The growth was performed in a H_2 atmosphere. In the LED samples the buffer GaN films for conventional and patterned sapphires were grown with the same growth process as described above. Details of the growth of the LED structure are described elsewhere.[18]

Contact-mode atomic force microscopy (AFM) was used to characterize the surface morphology and to determine the etch pit density (EPD) of the GaN template samples. For EPD measurements a selective etch was used to reveal TDs on the sample surface.[19] In this study a 1 : 1 mixture of hot 240 °C $H_2SO_4 : H_3PO_4$ was used as the selective etch. To evaluate the structural parameters of the GaN films and the LEDs the samples were analyzed with a high resolution X-ray diffraction (XRD) and SEM measurements. The room temperature (RT) and low temperature (LT) at 4 K PL spectra of the LED structures were measured by using a He–Cd laser (λ = 325 nm, power 20 mW) as an excitation source. LEDs with 440 × 440 μm² dimension were manufactured from the epi-wafers. The n-contact region was defined by plasma etching in order to expose the n-GaN layer. A transparent conductive oxide was used in order to favor current spreading in the p-GaN layer. In the electroluminescence (EL) measurements 500 individual chips on each wafer were probed and the EL was detected from both the top and bottom sides of the wafer.

Results

GaN films on pillar patterned sapphires

Fig. 1(c) and (d) show the SEM cross section images of the GaN films grown on LDPS and honeycomb PSSs, respectively. It can be seen that the GaN layer is grown on all facets of the PSS surface. As a result, the GaN layer completely fills the spacing between the pillars without any voids. In some parts of the wafers voids in the GaN film were observed on top of the pillars of the honeycomb substrates (Fig. 1(d)). The origins of these voids were the small hole patterns on top of the pillars in some parts of the wafers caused by the interference effect under the mask during the light exposure in the lithography process. The pillar depths in the LDPS substrates were relative low compared to depths with honeycomb substrates. The reason for this may be explained with the help of Fig.1(e). In the case of LDPS substrates the increasing pillar depths cause the fast growth of GaN rods originating from the crossroads of the sapphire crystal planes. These rods become a significant problem in terms of reasonable coalescence time of the GaN surface. No such problems appeared with honeycomb sapphires, so deeper pillar depths could be used.

The improvements in crystalline quality of GaN films using LDPS, honeycomb and CSs are summarized in Table 1, where the EPD, XRD and surface roughness data are summarized. The samples had a smooth surface morphology which can be observed from AFM scans in Fig. 2(a) and (b). To investigate the influence of the pattern type and depth on the TD density AFM EPD scans were taken from the template samples. Fig. 2(c) and (d) show the difference between the EPDs in the cases of CS and honeycomb sapphire, respectively. There exists a five-times difference between the TD density levels of 1.04×10^9 cm^{-2} and 2.1×10^8 cm^{-2} between these samples. The behavior of EPD as function of pillar depth is shown in the Fig. 3. for GaN films on both LDPS and honeycomb PSSs. The plot clearly shows that

Table 1 Crystal quality of the GaN films grown on reference CS, LDPS, and honeycomb substrates with various pillar depths

Substrate			XRD-FWHM (arc s)	
Mask	Depth (nm)	EPD (cm^{-2})	002	302
CS	—	1.0×10^9	12	192
LDPS	300	3.5×10^8	12	189
LDPS	550	3.8×10^8	14	184
LDPS	700	6.6×10^8	15	172
Honeycomb	500	2.2×10^8	13	198
Honeycomb	1050	2.1×10^8	13	145
Honeycomb	1300	2.6×10^8	14	181

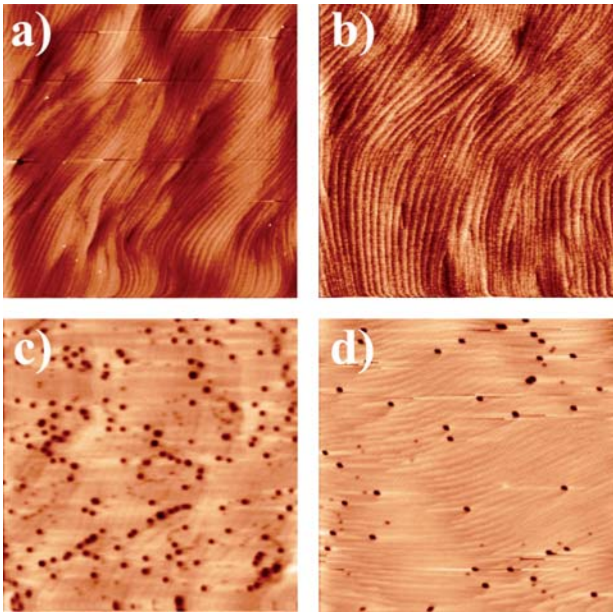

Fig. 2 5 × 5 μm² AFM surface scans of (a) a reference GaN template sample grown on CS and (b) a GaN template grown on honeycomb sapphire with pillar depth of 1050 nm. From both GaN surface scans a smooth surface and atomic steps can be observed. Scans (c) and (d) can be observed. Scans (c) and (d) illustrate the EPD on GaN layers grown on CS and on honeycomb sapphire with pillar depth of 1050 nm, respectively.

with the honeycomb pattern all pillar depths have significantly lower TD density compared to the case of CS. The minimum TD density is observed with 1050 nm pillar depth. In the case of LDPS the pillar depth is much more crucial. It can be observed that even as low as 300 nm pillar depth (Fig. 1(c)) decreases the TD density level to the nearly same level as in 500 nm depth honeycomb sapphire but then the TD density increases with the increase of the pillar depth. The reason for this behavior is obviously the mechanism of fast growing rods already described before. This mechanism makes growth of high quality GaN films more and more challenging with increasing pillar depths.

LED structures on pillar patterned sapphires

Fig.4. shows results of RT PL measurements from the samples grown on honeycomb sapphires. The optical properties of the LED samples are also summarized in the Table 2. It can be seen from the PL plot that all LED samples grown on honeycomb sapphires showed an enhanced PL intensity compared to the reference sample grown on CS. However, it can be noted from Table 2 that with LDPS LEDs only the sample grown on the substrate with the highest pillar depth of 700 nm shows a significantly higher PL intensity compared to the CS LED. We did not observe a correlation between the increased PL intensity and the reduction of the TD density. A more obvious correlation can be seen between increased PL intensity and increased pillar depth with LEDs grown on LDPS sapphires. It is obvious that when the pillar depth increases the ratio between the exceptional crystal planes compared to the area of the C-plane increases from 0.19 to 0.49. Thus an improved LEE can be observed with the increasing pillar depth. In the case of the honeycomb pattern an idea in the original design was to have higher area ratio from 0.7–1.25 between exceptional planes and the C-plane. For this reason the LEE of the LEDs grown on honeycomb sapphires is already high with 550 nm pillar depth and it is not increasing with increasing pillar depth. These results attribute that improvement of the PL intensity is mainly caused by the enhanced LEE. The increase in the PL efficiency in the majority of the samples is pretty high. In other studies it has been simulated and measured that ICP etched stripe patterns on the sapphire substrate cause an increase of over 20%.[15] In the case of chemically wet etched PSSs the increase of the LEE might be even higher because the sidewalls of the patterns are inclined unlike the almost vertical sidewalls of the ICP etched sapphire substrate.[10] For further clarification of the issue between IQE and LEE a temperature dependence of the integrated PL intensity of the honeycomb and reference samples was measured. Which is a common way to roughly estimate the IQE of the MQW structures.[8] The ratios between PL intensities of LT and RT measurements are also summarized in Table 2. It can be noted that only sample H-LED1 has an improved IQE while the other two honeycomb samples have actually a little bit lower IQE compared to the

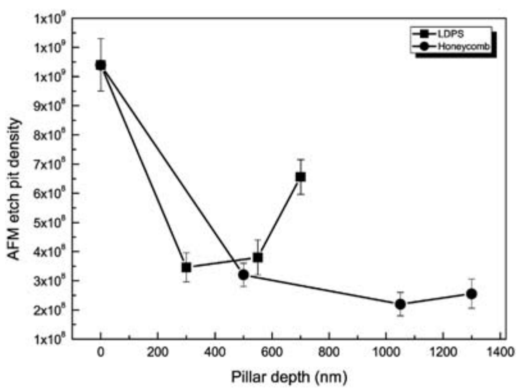

Fig. 3 AFM EPD of the samples grown on both pattern types (LDPS and honeycomb) with different pillar depths. Plot shows that PSSs offer lower density of dislocations with all pillar depths. However, the optimum depth depends on the pattern. With LDPS lower pattern depths are optimal.

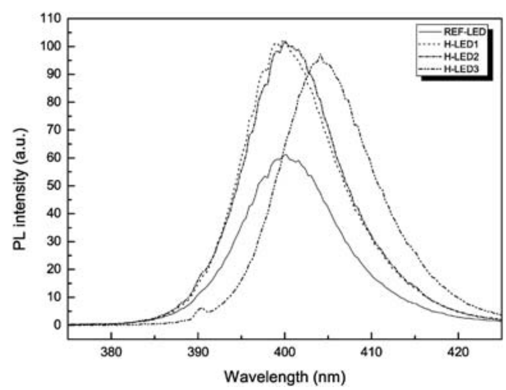

Fig. 4 PL intensities of the LED samples growth on honeycomb substrates. All the samples show higher PL intensity compared to the reference sample growth on CS. A 4 nm red shift of the sample H-LED3 compared to other samples is probably caused by run to run fluctuations. The PL peak intensity value of the sample H-LED1 is scaled to 100.

Table 2 Optical performance of the InGaN/GaN LEDs grown on CS, LDPS, and honeycomb substrates. The PL, top side EL, and bottom side EL intensity values of reference sample are scaled to 100. EL intensity values are averaged from the best 10% of the operating chips measured around each wafer. EPD values measured from GaN template samples have been inserted into the table for comparison

	Substrate			RT PL				EL int. at 20 mA			
Sample	Mask	Depth (nm)	Template EPD (cm^{-2})	Int. (a.u.)	λ (nm)	FWHM (nm)	RT/LT PL Ratio (a.u.)	Top side (a.u.)	Back side (a.u.)	λ (nm)	FWHM (nm)
REF-LED	CS	—	1.0×10^9	100	400	15	100	100	100	404	15
L-LED1	LDPS	300	3.5×10^8	98	409	15	—	116	110	410	16
L-LED2	LDPS	550	3.8×10^8	117	400	15	—	95	87	405	15
L-LED3	LDPS	700	6.6×10^8	162	406	16	—	93	81	408	16
H-LED1	Honeycomb	500	2.2×10^8	167	400	13	107	132	119	406	16
H-LED2	Honeycomb	1050	2.1×10^8	165	400	13	95	121	111	405	16
H-LED3	Honeycomb	1300	2.6×10^8	158	404	14	94	130	119	409	16

reference sample. However, all the IQEs are in the same range and there did not exist as big differences between patterned and non patterned samples as those observed in some studies.[8,15,16]

EL results are also summarized in Table 2. From these results it can be noted that the LED grown on the 300 nm deep LDPS sapphire which had a similar PL efficiency as the reference LED has higher EL output than the reference LED. However, in the case of the other LEDs grown on PSSs the increase of EL intensity is lower than the increase of PL efficiency. Samples L-LED2 and L-LED3 with an improved PL efficiency were actually showing a little bit lower EL output compared to the reference sample. However, TD densities in samples L-LED2 and L-LED3 were lower than in the reference sample. So the TD density does not explain the lower EL intensity. To further investigate the lower than expected EL intensity we took more SEM surface scans from these two samples. It was observed from these scans that the p-GaN surfaces in these samples contain small scale holes. These holes are probably originated from the more challenging coalescence process during the growth on LDPS sapphire. Some of these holes can act as a micro channels over the active region for carriers lowering the efficiency of the operating device. This also gives an explanation of why the PL intensities of these samples were so high considering that PL gives information on the material properties of the active region while EL is also influenced by the transport properties of the electrons and holes.

It is believed that TDs may act as a diffusion pathway for Mg which generates the electron path over the active region of LED and influence the EL emission efficiency.[8] It has also been stated that decreased TD density caused by the use of PSSs increases the EL efficiency.[5,6,8] Also it is supposed that in UV-LEDs the TDs might decrease the light output more due the limited self screening mechanism in InGaN/GaN quantum wells caused by lower In composition.[3,20] However, according to our results the enhanced LEE has the major role and the choice of the optimal patterning for the light extraction is the most important thing with PSS while the TD reduction effect from the level 10^9 cm^{-2} to the level 2×10^8 cm^{-2} has only a minor role.

Fig. 5 shows the measurement results of RT EL intensity as a function of driving current. The data was obtained from the best individual chips of the LEDs grown on the CS and honeycomb sapphire. It can be noted that the LED structure grown on honeycomb sapphire offers higher EL output intensity compared to the reference LED without exceptions over the whole current range. The top side output powers for honeycomb and conventional substrate are estimated to be 4.1 mW and 2.8 mW at 20 mA, respectively. However, one should remember that the differences between average values shown in Table 2. were not this high. There was no significant current dependent efficiency variation between the samples. Fig. 6 shows the *I–V* curve of the sample on the CS and honeycomb sapphire. Very low level forward voltages 3.24 V and 3.37 V were measured, respectively. The forward voltages in the LEDs grown on PSS were always a little bit higher than in the reference LED grown on CS as shown in Fig. 6. The reason for this behavior was found to be related to n-type material. Resistance values between n-type contacts of the chips next to each other were higher on the LEDs grown on the PSSs than on the CS. This indicates that the total volume of the low resistance n-type GaN is somehow decreased

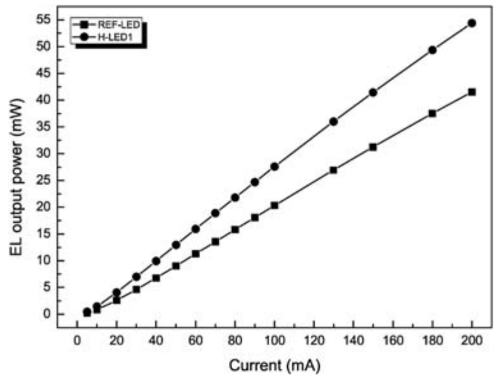

Fig. 5 EL output power as a function of driving current from the best individual chips of the samples H-LED1 grown on honeycomb substrate and REF-LED grown on standard sapphire. H-LED1 shows a higher EL output over the whole current range from 5 mA to 200 mA.

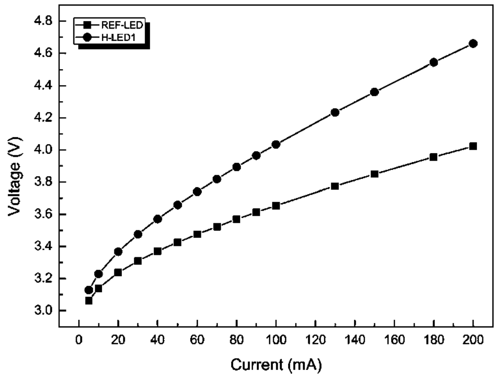

Fig. 6 Curves of current–voltage (*I–V*) of the LEDs H-LED1 grown on honeycomb substrate and REF-LED grown on CS. As can be seen from the plot sample H-LED1 had a little bit higher voltage values compared to the reference LED. Similar behavior was observed for all LED growth on pillar PSSs.

when the LED structure is grown on the PSS. In previous studies the forward voltages with PSSs have been reported to be lower, similar and higher compared to CSs.[8,13,16] According to our results the different n-type GaN thickness might have been one reason for the contradictory forward voltage behavior in the other studies.

Conclusions

High quality GaN templates and nitride-based LEDs were grown on various pillar PSSs fabricated by chemical wet etching. A five times decrease in TD density was observed from the GaN films grown on PSSs. Also the enhancement of the LED PL and average EL performances were observed. The growth on honeycomb PSSs was found to be straightforward but in the case of LDPS patterned sapphire the correct choice of the pillar depth was found to be crucial for high quality crystal growth. The enhanced LEE rather than improved material quality was found to cause the improvement in the LED performance.

Acknowledgements

This work was supported by the Multidisciplinary Institute of Digitalization and Energy (MIDE).

Notes and references

1 D. A. Steigerwald, J. C. Bhat, D. Collins, R. M. Fletcher, M. O. Holcomb, M. J. Ludowise, P. S. Martin and S. L. Rudaz, *IEEE J. Sel. Top. Quantum Electron.*, 2002, **8**, 310.
2 T. Mukai, T. Yamada and S. Nakamura, *Jpn. J. Appl. Phys.*, 1995, **37**, L1358.
3 A. Hangleiter, F. Hitzel, C. Netzel, D. Fuhrmann, U. Rossow, G. Ade and P. Hinze, *Phys. Rev. Lett.*, 2005, **95**, 127402.
4 I. Kidoguchi, A. Iishibashi, G. Sugahara and Y. Ban, *Appl. Phys. Lett.*, 2000, **76**, 3768.
5 A. M. Rokowski, P. Q. Miraglia, E. A. Prele, S. Einfeldt and R. F. Davis, *J. Cryst. Growth*, 2002, **241**, 141.
6 T. Lang, M. A. Odnoblyudov, V. E. Bougrov, A. E. Tomanov, S. Suihkonen, M. Sopanen and H. Lipsanen, *Phys. Status Solidi A*, 2006, **203**, R76.
7 Carol I. H. Ashby, Christine C. Mitchell, Jung Han, Nancy A. Missert, Paula P. Provencio, David M. Follstaedt, Gregory M. Peake and Leonardo Griego, *Appl. Phys. Lett.*, 2000, **77**, 3233.
8 D. S. Wuu, W. K. Wang, K. S. Wen, S. C. Huang, S. H. Lin, S. Y. Huang, C. F. Lin and R. H. Horng, *Appl. Phys. Lett.*, 2006, **89**, 161105.
9 S.-H. Park, H. Jeon, Y.-J. Sung and G.-Y. Yeom, *Appl. Opt.*, 2001, **40**, 3698.
10 Y. P. Hsu, S. J. Chang, Y. K. Su, J. K. Sheu, C. H. Kuo, C. S. Chang and S. C. Shei, *Opt. Mater.*, 2005, **27**, 1171.
11 S.-J. Kim, *Jpn. J. Appl. Phys.*, 2005, **44**, 2921.
12 H. S. Kim, J. S. Hwang and P. J. Chong, *J. Kor. Chem. Soc.*, 1995, **39**, 1.
13 Y. J. Lee, J. M. Hwang, T. C. Hsu, M. H. Hsieh, M. J. Jou, B. J. Lee, T. C. Lu, H. C. Kuo and S. C. Wang, *IEEE Photonics Technol. Lett.*, 2006, **18**, 1152.
14 X. Ding, T. Sato, Y. Kawaguchi and H. Niino, *Jpn. J. Appl. Phys.*, 2003, 42.
15 Y. J. Lee, T. C. Hsu, H. C. Kuo, S. C. Wang, Y. L. Yang, S. N. Yen, Y. T. Chu, Y. J. Shen, M. H. Hsieh, M. J. Jou and B. J. Lee, *Mater. Sci. Eng., B*, 2005, **122**, 184.
16 S. J. Chang, Y. C. Lin, Y. K. Su, C. S. Chang, T. C. Wen, S. C. Shei, J. C. Ke, C. W. Kuo, S. C. Chen and C. H. Liu, *Solid-State Electron.*, 2003, **47**, 1539.
17 M. Yamada, T. Mitani, Y. Narukawa, S. Shioji, I. Niki, S. Sonobe, K. Geguchi, M. Sano and T. Mukai, *Jpn. J. Appl. Phys.*, 2002, **41**, L1431.
18 O. Svensk, P. T. Törmä, M. Ali, S. Suihkonen, M. Soppanen, M. A. Odnoblyudov and V. E. Bougrov, *J. Cryst. Growth*, 2008, **310**, 5154.
19 X. Xu, R. P. Vaudo, J. Flynn and G. R. Brandes, *J. Electron. Mater.*, 2002, **31**, 402.
20 S. Suihkonen, O. Svensk, T. Lang, H. Lipsanen, M. A. Odnoblyudov and V. E. Bougrov, *J. Cryst. Growth*, 2007, **298**, 740.

