

CrossMark  
click for updatesCite this: *CrystEngComm*, 2014, 16, 8058

## Stress-induced *in situ* epitaxial lateral overgrowth of high-quality GaN

Xiaotong Liu,<sup>ab</sup> Dabing Li,<sup>\*a</sup> Xiaojuan Sun,<sup>\*a</sup> Zhiming Li,<sup>a</sup> Hang Song,<sup>a</sup> Hong Jiang<sup>\*a</sup> and Yiren Chen<sup>ab</sup>

We proposed a method, *i.e.*, stress-induced *in situ* epitaxial lateral overgrowth (ELO), for growing high-quality GaN heteroepilayers, and demonstrated its feasibility using both theory and experiment. Theoretical analysis by finite element simulation indicated that at a proper lattice mismatch, GaN islands formed during initial growth, continued to grow up to a stable state and finally coalesced into a film. To evaluate the effectiveness of the theoretical analysis, GaN films were grown on AlN/sapphire and GaN/sapphire templates. The experimental results showed that the stress at the interface between AlN and GaN initially caused separate GaN islands to form; subsequently, new islands stopped growing, and the islands displayed lateral growth until they coalesced into a film; however, GaN grown on GaN/sapphire always showed layer-by-layer growth, from the initial stage through to the final stage of growth. Therefore, the experimental results are consistent with the theoretical analysis, and stress-induced *in situ* ELO is a promising method for growing high-quality GaN films on suitable lattice-mismatched substrates, which is effective not only for growing GaN, but also for other lattice-mismatched epitaxial growth.

Received 13th May 2014,  
Accepted 16th June 2014

DOI: 10.1039/c4ce01003e

[www.rsc.org/crystengcomm](http://www.rsc.org/crystengcomm)

### 1 Introduction

Because of their wide band gap and good thermal and chemical stability, III-nitride structures are attractive for applications such as light-emitting diodes (LEDs), ultraviolet detectors, and high-power, high-frequency electronic devices.<sup>1–4</sup> Due to a lack of commercial homo-substrates, the growth of III-nitrides is mainly performed on mismatched sapphire substrates, leading to dislocation densities as high as  $10^8$ – $10^{10}$  cm<sup>-2</sup>. It has been proven that dislocations represent the main leakage pathway in GaN-based Schottky contacts,<sup>5–7</sup> and also act as nonradiative recombination centers and charge scattering centers in GaN-based optoelectronic devices.<sup>8,9</sup> Thus, the high dislocation density in III-nitrides represents an important limit for GaN-based electronic and optoelectronic devices with respect to their high potential for performance and reliability.

The question of how to obtain high-quality GaN-based materials is key for the GaN research community, and several efforts in the epitaxial field are producing important and encouraging results for the improvement of III-nitride quality. Epitaxial lateral overgrowth (ELO) is commonly used to

reduce the dislocation density in III-nitrides by bending and terminating some dislocations.<sup>10,11</sup> However, this method requires *ex situ* patterning, which makes the growth technique more complicated. Typically, a thin nucleation layer (NL) of GaN or AlN is used between the main GaN layer and the substrate. The growth conditions of such a NL – growth rate, V/III ratio, and reactor pressure – were demonstrated to strongly influence the structural quality of the GaN grown above. The role of the NL is considered to be reducing the interfacial energy between the GaN epilayer and the sapphire substrate. However, the growth kinetics need to be studied further and some mechanistic aspects are still not clear, such as why only GaN islands are obtained when GaN grows directly on a sapphire substrate without a NL.

Recently, a high-quality GaN layer was grown on an AlN/sapphire template. It is found that very few dislocations penetrate into the upper GaN layers,<sup>12</sup> however, the mechanism of the reduction in dislocations in GaN epilayers grown on AlN/sapphire templates is unclear. In this paper, we focus on the lattice mismatch between the epilayers and the substrates, and study the effect of lattice mismatch on the growth evolution of GaN using both theory and experiment. Based on crystal growth theory, we first calculated the evolution of GaN grown on different lattice-mismatched substrates using finite element analysis, which indicated that at a proper lattice mismatch, the growth of GaN underwent a transition from islands to a film, which could bend some dislocations. Then we evaluated these simulation results by growing GaN on

<sup>a</sup> State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Mechanics and Physics, Chinese Academy of Sciences, 3888 Dongnanhu Road, Changchun 130033, People's Republic of China. E-mail: lidb@ciomp.ac.cn, sunxj@ciomp.ac.cn, jiangh@ciomp.ac.cn

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

AlN/sapphire and GaN/sapphire template substrates, and our experimental results were consistent with the theoretical analysis. Based on these results, we propose a new growth method to obtain high quality GaN, *i.e.*, stress-induced *in situ* epitaxial lateral overgrowth. The idea proposed here can explain why high quality GaN films can be obtained on AlN/sapphire templates, and also why only GaN islands can be obtained on sapphire without a nucleation layer. The method is efficient not only for growing GaN, but also for other lattice-mismatched epitaxial growth.

## 2 Experimental

GaN was grown on AlN/sapphire templates by MOCVD at 1050 °C without first growing a low-temperature NL. Trimethylgallium (TMG) and ammonia (NH<sub>3</sub>) were used as the Ga and N precursors, respectively. For comparison, GaN was also grown on GaN/sapphire templates at 1050 °C. In both cases, the growth times were 1, 3, 5, and 10 min and the growth rate was the same for all samples, at about 40 nm min<sup>-1</sup>. Atomic force microscopy (AFM), photoluminescence (PL), a micro-Raman spectrometer in a back-scattering geometry configuration and high-resolution X-ray diffraction (HRXRD, Bruker D8) were used to characterize their structural and optical properties.

## 3 Results and discussion

Stress-induced *in situ* ELO is based on the principle that if the lattice mismatch is not large, *i.e.*, below 0.5%, then growth tends to be planar; if the mismatch is large, the material tends to gather into islands.<sup>13</sup> Whether the stress-induced islands form or not depends on the total change in free energy. If the net change in free energy is negative, then the islands will form spontaneously, but otherwise the islands may not form. The total free energy change is described as follows:<sup>13</sup>

$$\begin{aligned}
 F &= M\varepsilon^2V \int_{\hat{R}} \frac{1}{2} \hat{C}_{ijkl} \hat{\varepsilon}_{ij} \hat{\varepsilon}_{kl} d\hat{R} - M\varepsilon^2V + \pi \left( \frac{3V}{\pi a} \right)^{2/3} \left[ \gamma_c \sqrt{1+a^2} - \gamma_s \right] \\
 &= M\varepsilon^2V \left[ \hat{W}(a, \nu) - 1 \right] + \gamma V^{2/3} \hat{\Gamma}(a)
 \end{aligned}
 \tag{1}$$

Stress-induced islands are shown in Fig. 1(a). To consider a common phenomenon, we simplify the pyramidal island to a circular cone, where  $a$  is the ratio of the height  $h$  to the base radius  $r$ ,  $M$  is the biaxial modulus,  $\nu$  is the Poisson ratio,  $\hat{R}$  is the spatial region occupied by the islands,  $\hat{C}_{ijkl}$  is the elastic coefficient array,  $\hat{\varepsilon}_{ij}$  is the elastic strain field (which depends only on the lattice mismatch  $\varepsilon$ ), and  $\gamma$  is the energy density. The normalized total free energy change can be described as follows:

$$\frac{F}{M\varepsilon_m^2V} = \hat{W}(a, \nu) - 1 + \frac{\gamma}{M\varepsilon_m^2V^{1/3}} \hat{\Gamma}(a) = \hat{W}(a, \nu) - 1 + Z\hat{\Gamma}(a)
 \tag{2}$$

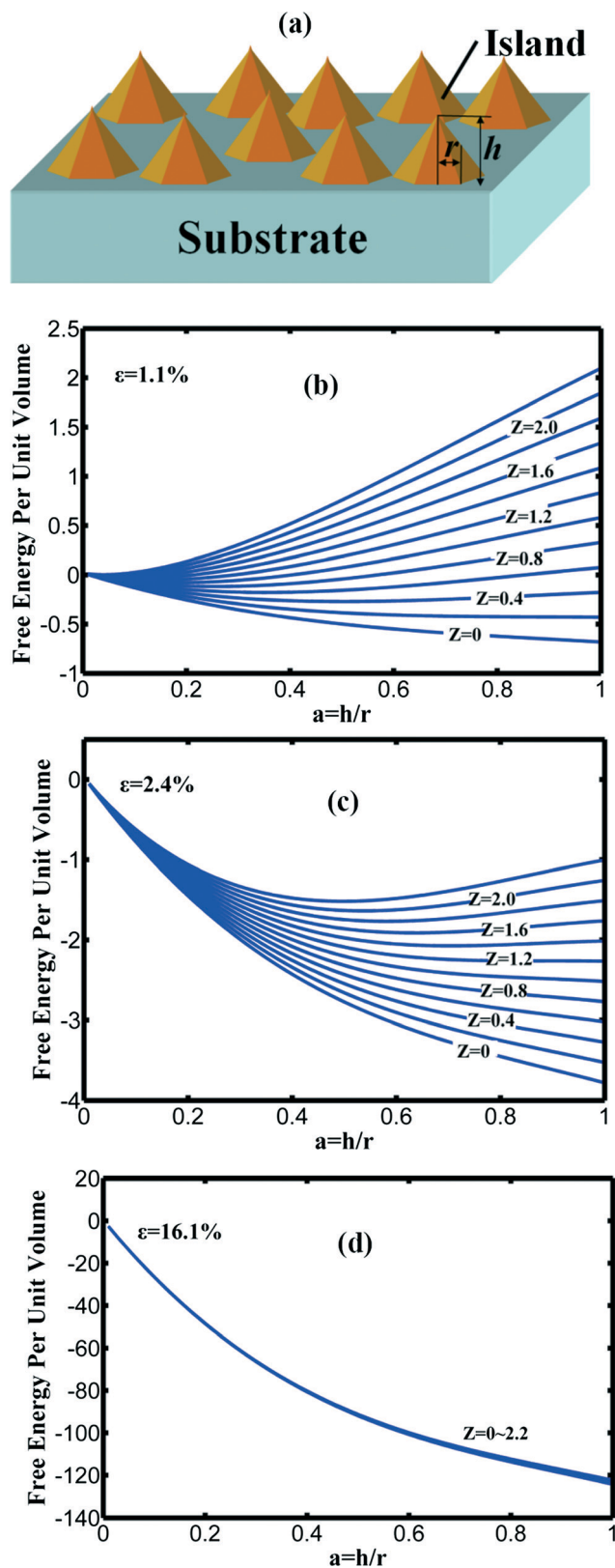


Fig. 1 Schematic illustration of the island structure (a) and the relationship between  $F/V$  and the ratio of the height ( $h$ ) to the base radius ( $r$ ),  $a$ , for GaN grown on heterosubstrates with different lattice mismatches,  $\varepsilon$ : (b) 1.1%, (c) 2.4%, and (d) 16.1%.

where the nondimensional ratio  $Z$  is defined as

$$Z = \frac{\gamma}{M \varepsilon_m^2 V^{1/3}}$$

We calculated the normalized free energy change per unit volume  $F/V$  by performing finite element analysis of GaN grown on heterosubstrates with different lattice mismatches ( $\varepsilon$ ). Fig. 1(b)–(d) show the relationship between  $F/V$  and the aspect ratio,  $a$ , for GaN grown on heterosubstrates with different lattice mismatches. For all the heterosubstrates,  $F/V$  decreased (expressed as a negative  $\Delta(F/V)$ ) initially as the height/base ratio increased, meaning that the GaN films were unstable and tended to form GaN islands. However, the  $\Delta(F/V)$  values of the three heterosubstrates differed greatly. The lattice mismatch  $\varepsilon$  followed the trend  $\varepsilon_{(b)} < \varepsilon_{(c)} < \varepsilon_{(d)}$  and  $\Delta(F/V)$  followed the trend  $\Delta F/V_{(b)} < \Delta F/V_{(c)} < \Delta F/V_{(d)}$ , suggesting that increasing the lattice mismatch  $\varepsilon$  led to GaN islands forming more easily. For the heterosubstrates with  $\varepsilon = 1.1\%$  and  $2.4\%$  (Fig. 1(b) and (c), respectively) every curve except for that with size parameter  $Z = 0$  had a local minimum, and thus a stable state for the GaN islands, after which the islands will coalesce into a film. However, for the heterosubstrate with  $\varepsilon = 16.1\%$  (Fig. 1(d)), the curves are all almost the same and none exhibit a local minimum. These results indicate that, while GaN islands formed most easily on the heterosubstrate with the largest lattice mismatch and thus the strongest interface stress, the islands have no stable state, meaning they will continue to grow without coalescing into a film, as the schematic in Fig. 2(c) shows. In this case, separate islands will form, which is consistent with previous experimental results where GaN was grown directly on sapphire,<sup>14</sup> and the same phenomenon was observed for AlN grown directly on sapphire substrates.<sup>15</sup> Comparing Fig. 1(b) and (c), when  $\varepsilon$  is too small

and thus the interface stress is too small, the stress-induced islands will coalesce easily because the stable state is attained during initial growth with little  $\Delta(F/V)$ , as shown in Fig. 1(b). In this case, especially for the GaN homoepitayer, the layer-by-layer growth mode will dominate the GaN growth process and the dislocations in the substrate will be propagated into the epilayer, as shown in Fig. 2(a).

At a suitable  $\varepsilon$ , as shown in Fig. 1(c), GaN islands will form during initial growth, continue to grow up to a stable state (consistent with the local minimum in Fig. 1(c)), and finally coalesce into a film. In this case, the growth mode transitions from three-dimensional island growth to quasi-two-dimensional layer-by-layer growth; this progression of *in situ* ELO bends or terminates some threading dislocations, leading to a high-quality GaN film, as shown in Fig. 2(b). Thus, it is easy to understand why the performance of GaN-based LEDs grown on AlN template substrates is sometimes better than that of those grown on GaN substrates when the substrates have the same dislocation density.

To evaluate our theoretical analysis, we grew GaN on  $1 \mu\text{m}$ -thick AlN/sapphire templates with  $\varepsilon = 2.4\%$  and on  $3 \mu\text{m}$ -thick GaN/sapphire templates with  $\varepsilon = 0$  for comparison. The FWHM of the (0002) and (10–12) planes is about 100 and 1000 arcsec for the AlN/sapphire template and about 270 and 483 arcsec for the GaN/template, respectively. Fig. 3(a)–(d) show AFM images of GaN grown on AlN/sapphire templates with growth times of 1, 3, 5, and 10 min, respectively. At a

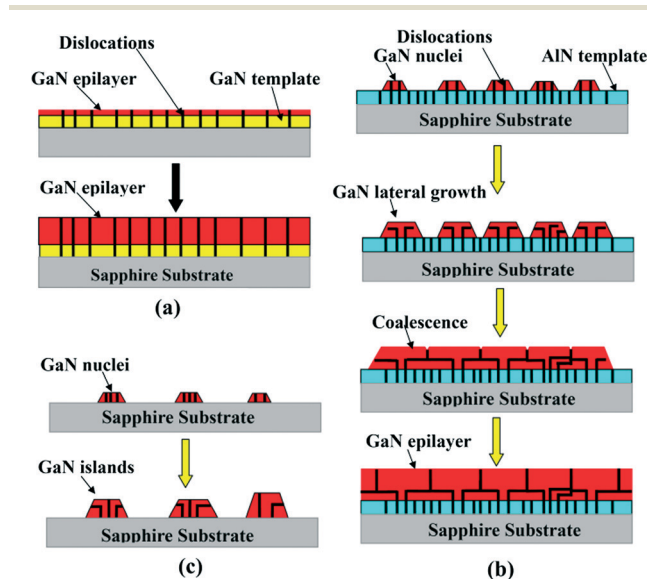


Fig. 2 Schematic for GaN grown on different lattice-mismatched substrates: (a) GaN/sapphire substrate, (b) AlN/sapphire substrate, (c) sapphire substrate.

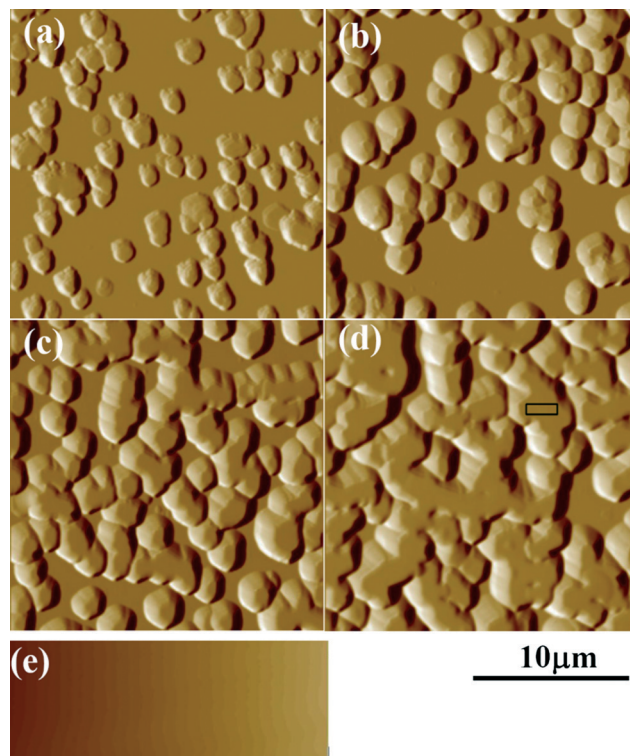


Fig. 3 AFM images of GaN grown on AlN/sapphire templates for different growth times and at a scale indicated by the black bar: (a) 1 min, (b) 3 min, (c) 5 min, (d) 10 min and (e) the enlarged AFM image of the selected area for 10 min growth.

growth time of 1 min (Fig. 3(a)), separate GaN islands grew initially on the AlN/sapphire template, confirming our theory that stress-induced GaN islands would spontaneously form when growing GaN on a heterosubstrate with  $\varepsilon = 2.4\%$ . At 3 min (Fig. 3(b)), rather than more islands forming, the GaN islands grew laterally. At 5 min (Fig. 3(c)), the GaN continued to experience lateral overgrowth, eventually causing the islands to coalesce, as shown at 10 min (Fig. 3(d)). This behavior also agrees with our theoretical analysis: at the stable state (at the local minimum in Fig. 1(c)), the islands will tend towards quasi-two-dimensional growth. These images, showing the evolution of GaN grown on AlN/sapphire templates, directly support the existence of stress-induced *in situ* ELO. Fig. 3(e) shows the enlarged surface morphology of GaN from Fig. 3(d), while Fig. 3(e) reveals clear and distinct atomic steps with terraces. AFM is often used to reveal dislocations in GaN epilayers, as researchers have shown that threading dislocations can cause surface depressions, step pins, and spiral growth hillocks. <sup>16,17</sup> Fig. 3(e) reveals no surface depressions, spiral growth hillocks, or pin steps, indicating that the GaN grown by stress-induced *in situ* ELO had a low dislocation density.

Fig. 4(a) and (b) compare the room-temperature micro-PL spectra of GaN grown for 1, 3, 5 and 10 min on AlN/sapphire templates and GaN/sapphire templates, respectively. For GaN grown on AlN/sapphire templates, the micro-PL spectral intensity of GaN increased with growth time and the PL intensity of GaN grown for 10 min was over five times greater than that of GaN grown for 5 min. The lowest PL intensity, for GaN grown for 1 min, occurred because the GaN islands were not yet covering the substrate, as shown in Fig. 3(a). As growth time increased, the GaN islands grew laterally and coalesced, increasing the PL intensity. As shown in the inset of Fig. 4(a), in all GaN PL spectra and over all growth times, we observed no yellow luminescence, which is defect-related. <sup>18,19</sup> In contrast, for GaN grown on GaN/sapphire templates, the intensities of the PL spectra remained nearly constant with growth time (Fig. 4(b)) and yellow luminescence near 550 nm was observed. This result indicates that the stress-induced *in situ* ELO method can effectively decrease the number of defects in GaN epilayers. Moreover, the FWHM of the GaN films grown by stress-induced *in situ* ELO was 180 arcsec for the (0002) plane and 290 arcsec for the (10-12) plane, while the FWHM of the GaN films grown on GaN/sapphire templates was 265 arcsec for the (0002) plane and 470 arcsec for the (10-12) plane. The FWHM of GaN epilayer grown on the GaN/Sapphire template was almost the same as that of the GaN/sapphire template, consistent with our theoretical analysis. The narrower FWHM for both the (0002) and (10-12) planes of GaN layers grown by stress-induced *in situ* ELO again confirms their high crystalline quality. <sup>9,20</sup> The thickness of the GaN layer is about 2.4  $\mu\text{m}$  on both AlN/sapphire and GaN/sapphire templates.

To study how the interface stress changed as the GaN islands grew, we used Raman spectroscopy. Fig. 5(a) shows Raman spectra of GaN grown on AlN/sapphire templates for various growth times. The  $E_2(h)$  phonon peak of GaN is

widely used to assess stress, because this frequency is very sensitive to biaxial strain in the  $c$ -plane and can be accurately measured using Raman spectroscopy. We used the  $419\text{ cm}^{-1}$  phonon peak of sapphire as a reference. These results reveal compressive stress in the GaN grown by stress-induced *in situ* ELO on the AlN/sapphire templates: the position of the  $E_2(h)$  phonon peak shifted to lower frequency as growth time increased, compared to the peak value of  $568\text{ cm}^{-1}$  for bulk GaN; increasing the growth time from 1 min to 10 min caused the  $E_2(h)$  phonon peak to shift from  $579\text{ cm}^{-1}$  to  $572\text{ cm}^{-1}$ . The relationship between the residual stress,  $N$ , and the shift of the phonon peak,  $\Delta W$ , is derived as follows: <sup>21</sup>

$$N = \frac{\Delta W}{K \times M}$$

where  $N$  is the stress,  $K$  is the linear stress-shift coefficient, and  $M$  is the biaxial modulus of GaN. We can deduce that the stress decreases with increasing thickness of the GaN epilayer and the stress is largest at the interface, which causes the GaN islands to form and is the driving force behind the *in situ*

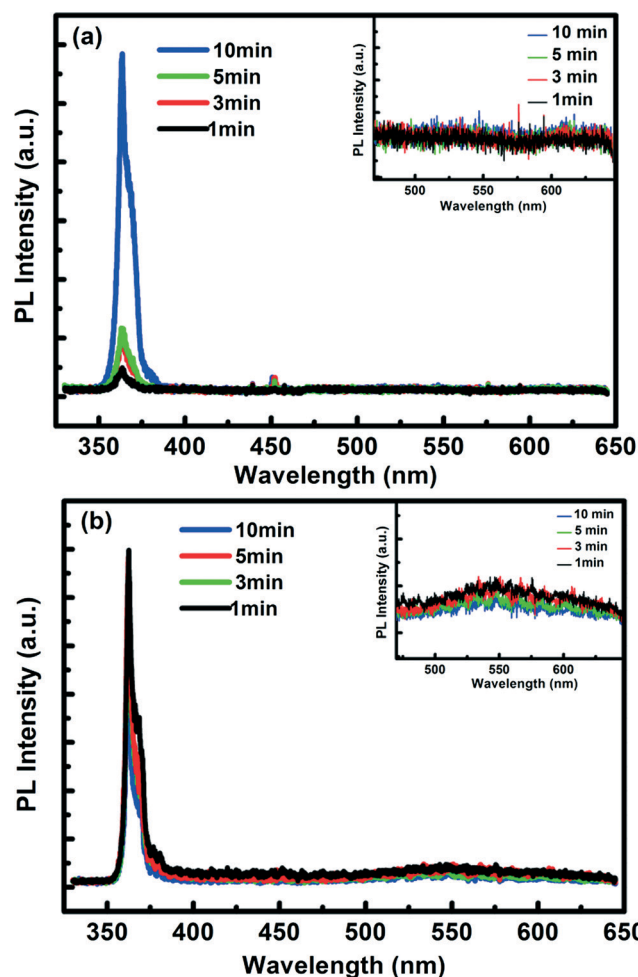


Fig. 4 Room-temperature micro-PL spectra of GaN grown for 1, 3, 5 and 10 min: (a) on AlN/sapphire templates and (b) on GaN/sapphire templates.

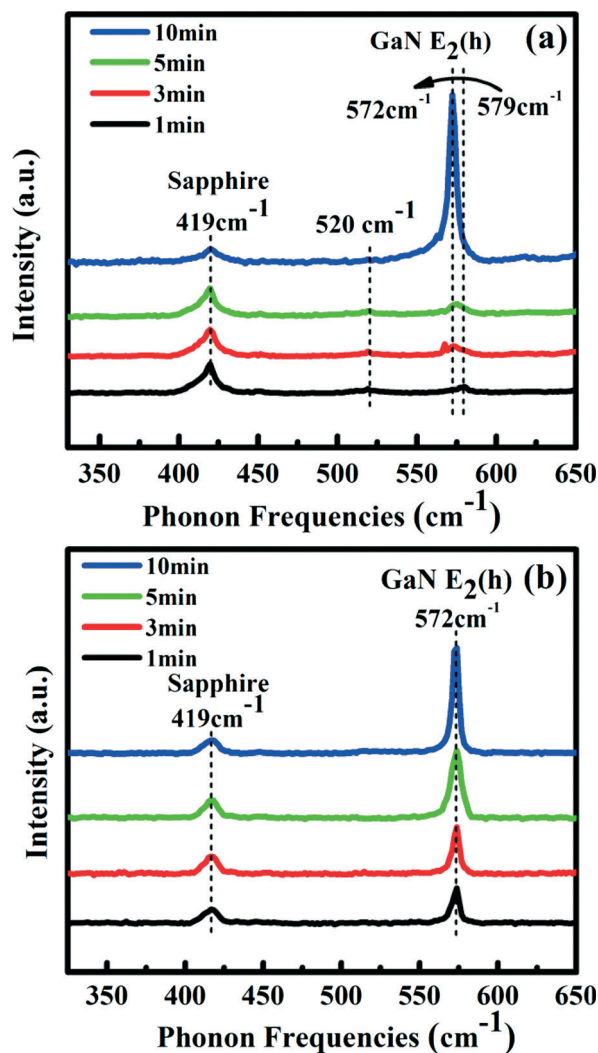


Fig. 5 Raman spectra of GaN grown for 1, 3, 5 and 10 min: (a) on AlN/sapphire templates (b) on GaN/sapphire templates.

ELO. In addition, the  $A_1$  (TO) peak at around  $520\text{ cm}^{-1}$  is observed in the Raman spectra of GaN grown on AlN/sapphire templates for 1, 3 and 5 minutes. According to the Raman selection rule, the appearance of the  $A_1$  (TO) peak indicates that instead of a planar GaN film, GaN islands are formed in the initial growth stage when GaN is grown by stress-induced ELO. The Raman spectra of GaN grown on GaN/sapphire templates are shown in Fig. 5(b). In contrast to the GaN grown on AlN/sapphire templates, the Raman spectra of GaN layers grown on GaN/sapphire templates showed no obvious shift of the  $E_2$  ( $h$ ) phonon peak and no appearance of the  $A_1$  (TO) peak, indicating that a planar GaN film was formed in the initial stage.

## Conclusions

In conclusion, we studied the growth kinetics of GaN on different lattice-mismatched substrates and proposed a growth method for heteroepitaxial GaN, stress-induced *in situ* ELO, demonstrating its potential through theory and experiment.

For GaN grown on the AlN/sapphire template, the stress at the interface initially caused separate GaN islands to form. Eventually, new islands stopped growing, and the islands that had formed grew laterally until they coalesced into a film. AFM images revealed these films to have smooth surface morphology with RMS of 0.1 nm; PL spectra exhibited no dislocation-related yellow luminescence, and XRD measurements revealed narrow FWHMs of 180 arcsec for the (0002) peak and 290 arcsec for the (10-12) peak. These results demonstrate that stress-induced *in situ* ELO produces high-quality GaN, and that the method is also promising for growing other heteroepitaxial layers.

## Acknowledgements

This work was partly supported by the National Key Basic Research Program of China (grant no. 2011CB301901), the National Natural Science Foundation of China (grant no. 61322406, 61274038, 61204070 and 51072195), the Jilin Provincial Science & Technology Department (grant no. 20140520116JH) and the open fund of State Key Laboratory of Luminescence and Applications (no. SKLLA201301).

## Notes and references

- 1 E. Matioli, S. Brinkley, K. M. Kelchner, Y. L. Hu, S. Nakamura, S. DenBaars, J. Speck and C. Weisbuch, *Light: Sci. Appl.*, 2012, 1, e22.
- 2 D. Li, X. Sun, H. Song, Z. Li, Y. Chen, H. Jiang and G. Miao, *Adv. Mater.*, 2012, 24, 845.
- 3 D. Li, X. Sun, H. Song, Z. Li, H. Jiang, Y. Chen and G. Miao, *Appl. Phys. Lett.*, 2011, 99, 261102.
- 4 T. Mizutani, H. Yamada, S. Kishimoto and F. Nakamura, *J. Appl. Phys.*, 2013, 113, 034502.
- 5 W. P. Hsu, M. J. Manfra, D. V. Lang, S. Richter, S. N. G. Chu, A. M. Sergent, R. N. Kleiman, L. N. Pfeiffer and R. J. Molnar, *Appl. Phys. Lett.*, 2001, 78, 1685.
- 6 J. E. Northrup, *Appl. Phys. Lett.*, 2001, 78, 2288.
- 7 W. Chikhaoui, J. M. Bluet, M. A. Poisson, N. Sarazin, C. Dua and C. B. Chevallie, *Appl. Phys. Lett.*, 2010, 96, 072107.
- 8 D. G. Zhao, D. S. Jiang, J. J. Zhu, Z. S. Liu, H. Wang, S. M. Zhang, Y. T. Wang and H. Yang, *Appl. Phys. Lett.*, 2009, 95, 041901.
- 9 D. B. Li, X. J. Sun, H. Song, Z. M. Li, Y. R. Chen, G. Q. Miao and H. Jiang, *Appl. Phys. Lett.*, 2011, 98, 011108.
- 10 M. D. Craven, S. H. Lim, F. Wu, J. S. Speck and S. P. DenBaars, *Appl. Phys. Lett.*, 2002, 81, 1201.
- 11 P. Fini, L. Zhao, B. Moran, M. Hansen, H. Marchand, J. P. Ibbetson, S. P. DenBaars, U. K. Mishra and J. S. Speck, *Appl. Phys. Lett.*, 1999, 75, 1706.
- 12 T. Egawa, H. Ohmura, H. Ishikawa and T. Jimbo, *Appl. Phys. Lett.*, 2002, 81, 292.
- 13 L. B. Freund and S. Suresh, *Thin film materials: stress, defect formation, and surface evolution*, Cambridge University Press, 2003, pp. 35 and 675.
- 14 S. Nakamura, *Jpn. J. Appl. Phys.*, 1991, 30, 1705.

- 15 X. Sun, D. Li, Y. Chen, H. Song, H. Jiang, Z. Li, G. Miao and Z. Zhang, *CrystEngComm*, 2013, 15, 6066.
- 16 E. Feltin, B. Beaumont, M. Laügt, P. de Mierry, P. Vennéguès, H. Lahrière, M. Leroux and P. Gibart, *Appl. Phys. Lett.*, 2001, 79, 3230.
- 17 W. B. Liu, D. G. Zhao, X. Sun, S. Zhang, D. S. Jiang, H. Wang, S. M. Zhang, Z. S. Liu, J. J. Zhu, Y. T. Wang, L. H. Duan and H. Yang, *J. Phys. D: Appl. Phys.*, 2009, 42, 015108.
- 18 R. Armitage, W. Hong, Q. Yang, H. Feick, J. Gebauer, E. R. Weber, S. Hautakangas and K. Saarinen, *Appl. Phys. Lett.*, 2003, 82, 3457.
- 19 F. A. Ponce, D. P. Bour, W. Götz and P. J. Wright, *Appl. Phys. Lett.*, 1996, 68, 57.
- 20 J. C. Zhang, D. G. Zhao, J. F. Wang, Y. T. Wang, J. Chen, J. P. Liu and H. Yang, *J. Cryst. Growth*, 2004, 268, 24.
- 21 H. Harima, *J. Phys.: Condens. Matter*, 2002, 14, 967.