Gradual variation method for thick GaN heteroepitaxy by hydride vapour phase epitaxy*

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Two strain-state samples of GaN, labelled the strain-relief sample and the quality-improved sample, were grown by hydride vapour phase epitaxy (HVPE), and then characterized by high-resolution X-ray diffraction, photoluminescence and optical microscopy. Two strain states of GaN in HVPE, like 3D and 2D growth modes in metal-organic chemical vapour deposition (MOCVD), provide an effective way to solve the heteroepitaxial problems of both strain relief and quality improvement. The gradual variation method (GVM), developed based on the two strain states, is characterized by growth parameters' gradual variation alternating between the strain-relief growth conditions and the quality-improved growth conditions. In GVM, the introduction of the strain-relief amplitude, which is defined by the range from the quality-improved growth conditions to the strain-relief growth conditions, makes the strain-relief control concise and effective. The 300-μm thick bright and crack-free GaN film grown on a two-inch sapphire proves the effectiveness of GVM.

Keywords: GaN, hydride vapour phase epitaxy, heteroepitaxy

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1. Introduction

In 1991, Nakamura succeeded for the first time in obtaining high-quality GaN films using low-temperature GaN as a buffer layer by metalorganic chemical vapour deposition (MOCVD).[1] The buffer layer method produced such a high-quality GaN that the two-step method prevails in the MOCVD-GaN heteroepitaxy. The idea of the two-step method successfully solved two basic problems confronted in heteroepitaxy, i.e. the strain relief and quality improvement. A low-temperature GaN layer was grown on sapphire as a buffer layer to accommodate the strain, on which high-quality GaN could be deposited at high temperatures.

Chen *et al.* reported high-quality AlN growth by MOCVD on SiC, having a multilayer structure that alternates between 3D and 2D growth modes.[2] This alternating way also made a balance between the strain release and the high crystal quality in heteroepitaxy, and produced crack-free and low dislocation thick AlN.

Hydride vapour phase epitaxy (HVPE) is a promising way to obtain bulk GaN,[3] because HVPE can grow GaN at hundreds of microns per hour, which is a much higher speed than that of MOCVD. At such a rapid growth rate, however, the HVPE becomes different from that of MOCVD, since the growth mode 3D and 2D is not as easy to control as that in MOCVD. Therefore, in HVPE, MOCVD grown templates are commonly used as starting substrates. If the growth mode in MOCVD templates has become 2D, the following HVPE-GaN will continue the 2D growth mode.[4]

In addition to quality consideration, strain relief is equally important owing to the problem of cracks in thick GaN heteroepitaxy by HVPE. Dam and coworkers[4] developed a way to grow 100–300 μm GaN

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without cracks with the aid of MOCVD templates. This strain relief way rested on MOCVD templates, which needed a gallium treatment step. However, it seemed that this strain-reduced technique depends on a MOCVD process rather than the following HVPE growth. Huang *et al.* reported that they obtained a 1.5-inch in diameter, 300-μm thick GaN film on a 2-inch sapphire without any crack.[5] The technique used to relax the residual stress was a dot air-bridged structure on the substrate, which involved a comparatively complicated pre-treatment.

In this study, a gradual variation method (GVM) is developed to solve HVPE problems of both strain relief and quality improvement. In order to make GVM easily understood, we first introduce two strain states of GaN in HVPE, namely the strain-relief state and the quality-improved state, which are similar to 3D and 2D growth modes in MOCVD. Then we present the design of GVM in which the GaN epitaxy is conducted gradually between the strain-relief state and the quality-improved state. We can see that GVM does not need any extra ex-site pre-treatment techniques and the entire strain relief process is performed along with the GaN growing process. Therefore, GVM is a simple and easy way for thick crystal growth.

2. Experiments

GaN crystals were grown in a vertical HVPE reactor with metallic gallium (Ga), hydrochloric acid (HCl) and ammonia (NH_3) as sources. Templates with 3-μm GaN layer grown by MOCVD on 430-μm thick sapphires were employed as starting substrates for HVPE growth. HCl reacted with metallic Ga at 900°C forming GaCl that was carried to the growth zone to react with NH_3 on the substrate surface for GaN crystal growth. The GaN growth temperature was 990°C–1080°C, the reactor pressure was 250–500 Torr (1 Torr = 133.3 Pa), and the V/III ratio 20–90. The ambience of the carrier gas was a mixture of H_2 and N_2.

When growth conditions in HVPE are optimized, we observe that heteroepitaxial GaN has two strain states, the strain-relief state and the quality-improved state. GaN in the strain-relief state has smaller strain and wider X-ray diffraction rocking curves than that in the quality-improved state.

In heteroepitaxial GaN, the two strain states of GaN depend on different growth conditions. In terms of kinetics, the growth state is determined by the diffusion length of adatoms on the surface. Generally speaking, higher temperature and lower V/III ratio will increase the adatom diffusion length, thereby increasing the lateral growth rates.[2] This enables a full coalescence of GaN in the lateral direction, leading to the GaN in the quality-improved state. While in reverse growth conditions, the adatom diffusion length is not enough for GaN to coalesce completely, leaving high dislocations inside the as-grown GaN. We know that dislocations can relieve the strain induced by lattice mismatch and the corresponding GaN is in the strain-relief state.

The GaN samples both in the two strain states, each with a thickness of 20 μm, were produced by HVPE. After growth, these samples were characterized by high-resolution X-ray diffraction (HR-XRD), photoluminescence (PL) and optical microscopy, proving that GaN in strain-relief state is of little strain but with a rough surface, and GaN in quality-improved state is mirror-like with narrow XRD rocking curves.

In the following measurements two typical samples, labelled as the strain-relief sample and the quality-improved sample, were used as representative of all samples in the two strain states, making the comparison between the two strain states simple and clear. The growth conditions for the strain-relief sample were 1000°C, 400 Torr, NH_3 2500 sccm and HCl 50 sccm, and for the quality-improved sample were 1070°C, 400 Torr, NH_3 800 sccm and HCl 20 sccm.

3. Results and discussion

3.1. Characterization of GaN in the two strain states

The strain-relief sample and the quality-improved sample were measured by HR-XRD in a Philips X'Pert MRD system with Cu $K\alpha_1$ line ($\lambda = 0.154056$ nm) as X-ray source. To measure the strain in the two samples, 2θ–ω scan in both (002) and (004) were measured. As shown in Fig. 1, the peak of the strain-relief sample has a clear right-shift compared with that of quality-improved sample in the (002) scan.

Considering the peak position error which is denoted by δ, the Bragg's law is transformed to

$$\begin{aligned} 2d_{(002)}\sin(\theta_{(002)}+\delta) &= 2d_{(004)}\sin(\theta_{(004)}+\delta) \\ &= \lambda_{\mathrm{Cu}K\alpha 1}. \end{aligned} \quad (1)$$

The data of both (002) and (004) could eliminate most of the peak position error. The calculated data of the two samples are presented in Table 1.

Table 1. Data of peaks in the two samples and the corresponding lattice constant c.

	Peak of 2θ in (002) scan/(°)	Peak of 2θ in (004) scan/(°)	Calculated δ/(°)	Corresponding c value/nm
Strain-relief sample	34.5487	72.8646	–0.0012	0.51885
Quality-improved sample	34.5448	72.8496	–0.0032	0.51896

We take $c_0 = 0.51852$ nm as the standard c value of free-strain GaN.[6] With the anisotropic elastic constants of GaN,[7] the relationship between stress and strain could be expressed as

$$\begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \end{bmatrix} = \begin{bmatrix} 390 & 145 & 106 \\ 145 & 390 & 106 \\ 106 & 106 & 398 \end{bmatrix} \begin{bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \end{bmatrix}. \quad (2)$$

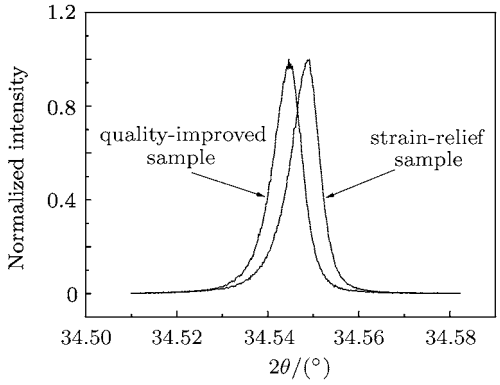


Fig. 1. 2θ–ω scans of (002) in both the strain-relief sample and the quality-improved sample.

According to the biaxial stress model, we have $\sigma_{xx} = \sigma_{yy}$, $\sigma_{zz} = 0$, $\varepsilon_{xx} = \varepsilon_{yy}$. Thus, the stress in the strain-relief sample and the quality-improved sample could be obtained. For the strain-relief sample, $\sigma_{xx} = \sigma_{yy} = -0.57$ GPa, and for the quality-improved sample, $\sigma_{xx} = \sigma_{yy} = -0.76$ GPa.

After 20 μm growth, the stress in the strain-relief sample is reduced by 25%, compared with the quality-improved sample.

Differences between the full width at half maximum (FWHM) of rocking curves in two samples are shown in Figs. 2(a) and 2(b). For the (002) plane, the FWHM of the strain-relief sample is 593″, compared with only 168″ of that in quality-improved sample, showing that the former GaN includes much more screw-type (screw and mixed) dislocations than the latter. In addition, for the (102) plane, the FWHMs are 580″ and 410″ respectively. The comparison in FWHMs implies that the strain can be reduced a lot by the formation of dislocations.[8–10]

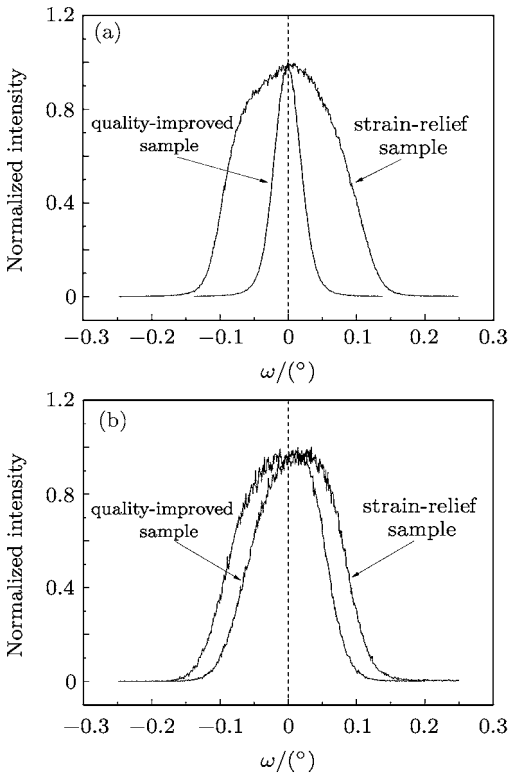


Fig. 2. FWHM comparisons between the two samples in rocking curves of (a) the (002) plane and (b) the (102) plane.

The PL spectra of the two samples are shown in Fig. 3. The dashed line (3.397 eV) shows the peak position of the PL line for a completely relaxed GaN bulk layer at room temperature.[11,12] The stress of 1.0 GPa would shift the near-band-edge PL line by 34 meV at room temperature.[12–14] It is found that the strain-relief sample has a blue shift of 19 meV, which corresponds to 0.56 GPa compressive stress; while in the quality-improved sample the shift is 27 meV, which corresponds to 0.79 GPa. According to PL measurement, after 20 μm growth the stress in the strain-relief sample is reduced by 29% as compared with those in the quality-improved sample. These results are in good agreement with HR-XRD results.

The surface morphologies of the strain-relief sample and the quality-improved sample are also studied by optical microscopy as shown in Fig. 4. As can be clearly seen from optical micrographs with Nomarski contrast, the surface morphology of the strain-relief

sample is rough (Fig. 4(a)), while that of the quality-improved sample is smooth and mirror-like (Fig. 4(b)). It is likely that it is the many dislocations that make the surface of strain-relief sample rough.

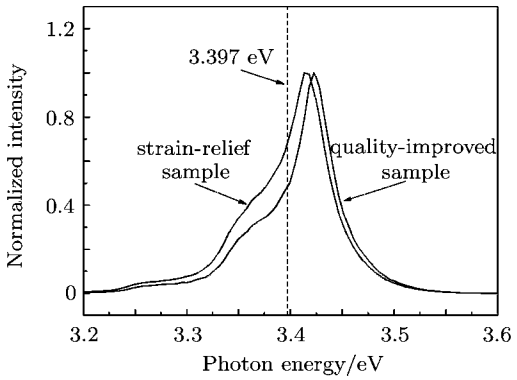


Fig. 3. Room temperature photoluminescence spectra of the strain-relief sample and the quality-improved sample.

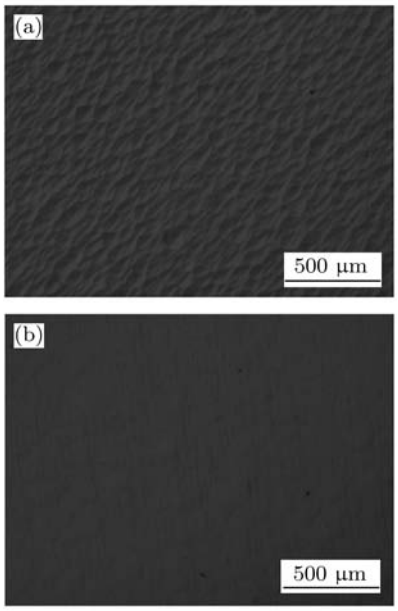


Fig. 4. Optical micrographs with Nomarski contrast of (a) the strain-relief sample and (b) the quality-improved sample.

As discussed above, HR-XRD, PL and optical microscopy measurements prove that the strain-relief sample and the quality-improved sample are in the true sense of their names. Thus, it can be concluded that strain-relief growth conditions can effectively relax the heteroepitaxial strain and quality-improved growth conditions are able to play the role of quality improvement.

It should be noted that the strain-relief state and the quality-improved state are introduced as two comparative concepts which will make Section 3.2 clear and easily understood. And this section has confirmed that GaN in the strain-relief state and the quality-improved state can be obtained by the corresponding growth conditions.

3.2. Gradual variation method for thick HVPE-GaN heteroepitaxy

If the thickness of GaN is limited to dozens of microns, probably the quality-improved sample itself could meet the requirement. However, for hundreds-of-microns thick GaN growth, the case is different. Prolonged growth of GaN in the quality-improved state leads to too much stress concentration resulting in cracks. When GaN in the strain-relief state keeps growing, the surface will become yellow or dark and full of hexagonal hillocks and V-shaped pits. Therefore, the strain-relief state or the quality-improved state alone cannot sustain long period enough to allow very thick GaN heteroepitaxy. However, the collaboration of the two strain states of GaN provides potential for very thick GaN growth.

As shown in Fig. 5, the gradual variation method (GVM) is introduced to solve HVPE problems of both strain relief and quality improvement, which allows thick crack-free GaN heteroepitaxy.

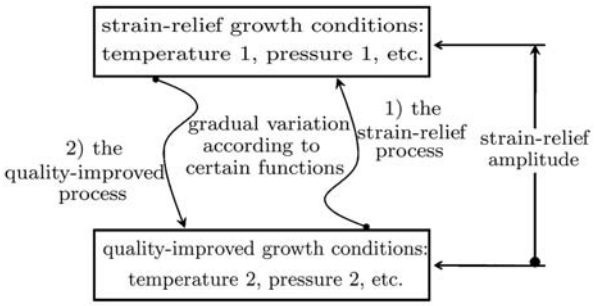


Fig. 5. The design of the gradual variation method.

The gradual variation alternating between strain-relief growth conditions and quality-improved growth conditions can work as two basic processes: 1) the strain-relief process, and 2) the quality-improved process. The strain-relief process should not last so long that the GaN produced is of such bad quality that it cannot be improved. Then the quality-improved process follows. Similarly, the quality-improved process should not continue so long that too much stress concentration results in cracks. Then the strain-relief process should follow. Thus, the regular alternation between the strain-relief process and the quality-improved process forms GVM which allows thick crack-free GaN heteroepitaxy.

It should be pointed out that gradual variation could be performed according to certain functions such as linear functions to make the change regular and logical. To be specific, the flow rate of HCl can be gradually modulated from 50 sccm to 20 sccm with a reduction of 1 sccm every minute. Other growth conditions like temperature can also be adjusted in this way although the accurate control over temperature is probably not easy.

Figure 6 illustrates the cross-sectional cathodoluminescence (CL) image of the heteroepitaxial HVPE-GaN by the GVM. The strain-relief process and the quality-improved process are evidently displayed by the alternation between the brightness and the darkness in the CL contrast, which is associated with the change of the number of dislocations. The CL spectra directly prove that the strain-relief process and the quality-improved process are in the true sense of their names.

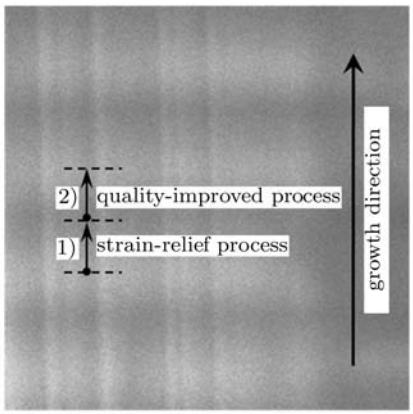


Fig. 6. The cross-sectional CL image of the heteroepitaxial HVPE-GaN by the GVM.

It is known that abrupt transitions in growth conditions can bring about interfaces where dislocations and faults originate easily. In a gentle and mild way, GVM allows the growth to be stable enough to largely eliminate defects. In what follows, the introduction of the strain-relief amplitude of GVM provides an effective way for strain-relief control to prevent film cracks.

Strain-relief growth conditions are different from quality-improved growth conditions. As mentioned in Section 2, the growth parameters for each of the two strain states, if set in a suitable growth window, have reverse tendencies. Therefore, the range from the quality-improved growth conditions to the strain-relief growth conditions can be defined as the strain-relief amplitude. The strain-relief amplitude can work as an effective indicator to adjust growth parameters. If the grown GaN is yellow or dark and full of hexagonal hillocks and V-shaped pits, which means bad crystal quality, what we should do next is to lessen the strain-relief amplitude. If the grown GaN is bright but cracked, which means too much residential stress in the epilayer, we need to increase the strain-relief amplitude. Thus, the balance between strain relief and crystal quality can be easily kept by regulating the strain-relief amplitude.

According to the GVM design for the thick GaN growth and relying on the effective adjustment of the strain-relief amplitude, we obtained two-inch 300-μm thick GaN on sapphire as shown in Fig. 7. The film is transparent, bright, and crack-free. Although the wafer is bowed, no crack is visible in either GaN epitaxial layer or sapphire substrate. This proves that the strain release in the thick epilayer is pretty good. The rocking curve FWHM value of the sample for the (002) plane is 133″, showing high quality of the epilayer. Therefore, the design of GVM for thick GaN heteroepitaxy is proved to be effective.



Fig. 7. Two-inch 300-μm thick crack-free GaN on sapphire.

The GVM in HVPE achieves the good effect of heteroepitaxy in the same way as the two-step method in MOCVD. In the two-step method of MOCVD, the 3D and 2D growth modes are used to balance the strain relief and crystal quality in heteroepitaxy. In GVM of HVPE, the strain-relief process and the quality-improved process work in a similar way. We know that the heteroepitaxial thickness of GaN in MOCVD is only several microns while that in HVPE reaches up to millimeters. Therefore, it is reasonable to extend the two-step method in MOCVD to the GVM in HVPE, which can be thought of as hundreds of steps arranged in a logical way. The idea of

GVM sheds new light on crystal heteroepitaxy and the mechanism of GVM needs to be further explored.

4. Conclusion

In different growth conditions by HVPE, GaN in the strain-relief state and the quality-improved state can be obtained, which is proved by the measurements of two typical samples of HR-XRD, PL and optical microscopy. Based on the strain-relief state and the quality-improved state, the gradual variation method (GVM) is introduced. The gradual variation alternating between the strain-relief growth conditions and the quality-improved growth conditions can work as the quality-improved process and the strain-relief process. The strain-relief amplitude, as the adjustment indicator, makes the strain relief concise and effective.

The growth of 300-μm thick GaN on sapphire proves the effectiveness of GVM for thick GaN heteroepitaxy. GVM does not need any extra ex-site pretreatment techniques and the entire strain relief process is performed along with the GaN growing process. Therefore, GVM is a simple and effective method which could be applied to thick film or bulk crystal growth.

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References

[1] Nakamura S 1991 *Jpn. J. Appl. Phys.* Part 2 **30** L1705

[2] Chen Z, Newman S, Brown D, Chung R, Keller S, Mishra U K, Denbaars S P and Nakamura S 2008 *Appl. Phys. Lett.* **93** 191906

[3] Fujito K, Kubo S, Nagaoka H, Mochizuki T, Namita H and Nagao S 2009 *J. Crystal Growth* **311** 3011

[4] Dam C E C, Grzegorczyk A P, Hageman P R and Larsen P K 2006 *J. Crystal Growth* **290** 473

[5] Huang H H, Chao C L, Chi T W, Chang Y L, Liu P C, Tu L W, Tsay J D, Kuo H C, Cheng S J and Lee W I 2009 *J. Crystal Growth* **311** 3029

[6] Darakchieva V, Monemar B, Usui A, Saenger M and Schubert M 2008 *J. Crystal Growth* **310** 959

[7] Polian A, Grimsditch M and Grzegory I 1996 *J. Appl. Phys.* **79** 3343

[8] Funato K, Hashimoto S, Yanashima K, Nakamura F and Ikeda M 1999 *Appl. Phys. Lett.* **75** 1137

[9] Lee S N, Son J K, Paek H S, Sakong T, Lee W, Kim K H, Kim S S, Lee Y J, Noh D Y, Yoon E, Nam O H and Park Y 2004 *Phys. Stat. Sol.* (c) **1** 2458

[10] Tyagi A, Wu F, Young E C, Chakraborty A, Ohta H, Bhat R, Fujito K, DenBaars S P, Nakamura S and Speck J S 2009 *Appl. Phys. Lett.* **95** 251905

[11] Song T L, Chua S J, Fitzgerald E A, Chen P and Tripathy S 2003 *Appl. Phys. Lett.* **83** 1545

[12] Wu J, Han X, Li J, Li D, Lu Y, Wei H, Cong G, Liu X, Zhu Q and Wang Z 2005 *J. Crystal Growth* **279** 335

[13] Kisielowski C, Kruger J, Ruvimov S, Suski T, Ager III J W, Jones E, Liliental-Weber Z, Rubin M and Weber E R 1996 *Phys. Rev.* B **54** 17745

[14] Lee K J, Shin E H, Shim S K, Kim T K, Yang G M and Lim K Y 2005 *Phys. Stat. Sol.* (c) **2** 2104