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# Influence of the misorientation of 6H–SiC substrate on the quality of GaN epilayer grown by MOVPE

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ABSTRACT

The effect of misorientation of 6H–SiC substrate on the structural quality of GaN epilayer grown by organometallic vapor phase epitaxy (MOVPE) has been investigated. The results reveal that the structural quality of GaN epilayer is significantly influenced by the misorientation of 6H–SiC substrate. Larger misorientation angle of 6H–SiC substrate results in better structural quality of GaN epilayer, such as narrower atomic step widths of GaN surface, less yellow luminescence band/edge emission ($I_y/I_b$) ratio of PL, and lower dislocations density. It is also found that the $I_y/I_b$ ratio of GaN epilayer is affected only by the misorientation angle of 6H–SiC substrate, but the screw dislocation density and edge dislocation density are influenced by both the misorientation angle and the misorientation direction of 6H–SiC substrate. GaN epilayer grown on 6H–SiC substrate with 2.3° misorientation angle towards $[1\,1\,\bar{2}\,0]$ direction has the best structural quality.

## 1. Introduction

In recent years, nitride semiconductors have been considered as the most promising materials for optoelectronic and high power electronic devices in general lighting and microwave applications [1–7]. Due to the lack of affordable large area GaN substrates, sapphire ($Al_2O_3$) [8,9], silicon carbide (SiC) [10,11] and other foreign substrates [12–14] are widely used for nitrides epitaxy growth. Between those substrates, SiC has been widely used because it has very high thermal conductivity and relatively small lattice mismatch with GaN [15]. Cree has broken 200 lm/W barriers in white LED chip using SiC substrate in the year 2009 [16]. Due to the lattice mismatch between GaN and SiC, GaN epilayer grown on SiC has high density of defects, such as threading dislocations (TDs) and unintentional doping levels. Threading dislocations density in GaN grown by MOVPE is commonly in a range of $10^8$–$10^{10}$/cm$^2$. It has been found that TDs degraded optoelectronic device properties and affected the reliability of electronic devices [17].

In most of early work, on-axis cut SiC wafers have been mostly used as the substrates of GaN epitaxial growth, especially in the field of light emitting diode production [15,18,19]. Early reports [15] showed that an ideal on-axis SiC surface without steps should allow the nucleation and the growth of a nearly perfect two-dimensional film. Recently, SiC substrates with misorientation have attracted many attentions. Many works have been done to reveal the impact of SiC substrate misorientation on the structural quality of GaN epilayer [15,18–22], but the conclusion is still unclear. Xie et al. found that the density of dislocations was reduced by one or two orders in GaN epilayer grown on 4H–SiC substrate with certain misorientation [20]. Kakanakova-Georgieva et al. obtained the similar result from AlN epilayer grown on off-axis SiC substrate [21]. Huang et al. studied the impact of off-axis substrate on the strain of GaN epilayer and found that the SiC substrate with a certain misorientation angles could help to control strain relaxation [22]. In contrast, some reversed results were reported. Bassim et al. found that the density of dislocations with c-component could be decreased in GaN epilayer by using on-axis substrate [18,19]. Rudziński et al. investigated the misorientation of 4H–SiC substrates on the morphology and crack of GaN epilayer, and obtained crack-free and high structural quality GaN grown on on-axis 4H–SiC [15].

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**Table 1**
The illustration of the five samples.

| | Misorientation angle | Misorientation direction |
|---|---|---|
| Sample A | 0° | – |
| Sample B | 0.9° | $[1\bar{1}00]$ |
| Sample C | 2.3° | $[1\bar{1}00]$ |
| Sample D | 0.7° | $[11\bar{2}0]$ |
| Sample E | 2.3° | $[11\bar{2}0]$ |

To further improve the performance of GaN devices, it is important to understand in principle the influence of misorientation of SiC substrate on the structural quality of GaN epilayer. Earlier research works about the effect of substrate misorientation only focused on the misorientation angle, the misorientation direction was ignored. Moreover, only dislocations density in the epilayer has been studied to characterize the structural quality. The yellow luminescence band/edge emission ($I_y/I_b$) ratio of PL has not been investigated. In this study, the influence of the misorientation angle and misorientation direction of 6H–SiC substrate on the $I_y/I_b$ and dislocations density of GaN epilayer were investigated systematically.

## 2. Experimental

GaN/AlN/SiC heterostructures were grown by MOVPE system. Trimethylaluminum (TMAl), trimethylgallium (TMGa) and ammonia ($NH_3$) were used as precursors. The growth pressures were 500 Torr and 100 Torr for GaN and AlN growth, respectively, to reduce parasitic chemical reactions. The growth temperatures were about 1070 °C and 1100 °C for GaN and AlN, respectively. The thicknesses of the AlN buffer layer and the GaN epilayer were about 10 nm and 4.0 μm, respectively [23].

Five 6H–SiC substrates with different misorientations were supplied by Shandong University, and all the five samples were grown in the same growth run. The details of the samples are listed in Table 1.

The band/edge and yellow luminescence emissions were evaluated by photoluminescence (PL) spectrum with 325 nm He–Cd laser. The surface morphology was examined by atom force microscope (AFM). The structural quality of the samples was also assessed by high resolution X-ray diffraction. After the evaluation by PL spectrum and AFM, all the samples were cut into two parts. Ones were etched in molten eutectic of KOH–NaOH for 15 min at the temperature of 450 °C to observe the density of etch pits; the others were over-etched in hot phosphoric acids for 15 min at 200 °C to analyze the erosion character. After etching, samples were examined by scanning electron microscope (SEM) and energy dispersive spectroscope (EDX).

## 3. Results and discussion

The surface morphologies of GaN epilayer for the five samples were observed by AFM and shown in Fig. 1. From the pictures, we can see that the surface morphologies of GaN epilayer were greatly influenced by the misorientation of 6H–SiC substrate. The surface atomic step widths of GaN epilayer for samples A, B, C, D, and E were 280 nm, 100 nm, 85 nm, 125 nm, and 40 nm, respectively. The atomic step width of GaN epilayer decreased with the increase of 6H–SiC substrate misorientation. The terrace step of sample A was the widest while samples C and E had the narrowest step width. For all samples, GaN epilayer had the same step heights of about 0.5 nm which corresponded to a stack period of wurtzite GaN along the *c*-axis and was not affected by the substrate misorientation. Therefore, only step width of GaN epilayer was affected by the misorientation of 6H–SiC substrate.

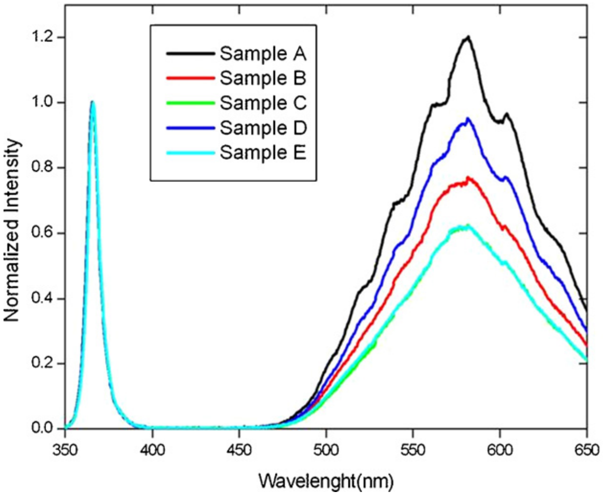

**Fig. 2.** Photoluminescence spectra of the five GaN samples.

Fig. 2 shows the photoluminescence spectra of the five samples. A band/edge emission and a yellow luminescence peak were observed in all samples. However, the intensities of the two emissions were different for each sample. Some researchers have reported that the yellow luminescence peak of GaN was related to some point defects, such as Ga vacancy ($V_{Ga}$) [24]. Recent results also suggested that the yellow luminescence actually originates from background carbon [25,26]. However, the intensity ratios of the yellow band to the band/edge emission ($I_y/I_b$) could be considered as a parameter to indicate the quality of GaN epilayer.

The band/edge emission intensity of all five samples were normalized to be 1, the $I_y/I_b$ ratio of samples A, B, C, D and E were 1.20, 0.75, 0.60, 0.95, and 0.60, respectively, indicating that the misorientation angle of substrate had significantly impacts on the optical quality of GaN films. Sample A with no misorientation had the largest $I_y/I_b$ ratio, and the yellow luminescence peak intensity was even higher than the band/edge emission intensity. The misorientation of substrate for samples D and B are 0.7° and 0.9°, respectively, which are larger than that for sample A. The $I_y/I_b$ ratios for both samples were decreased successively. The misorientation of SiC substrate for samples C and E are the same of 2.3°, the $I_y/I_b$ ratios of the two samples were also the lowest. The results showed that the $I_y/I_b$ ratio could be reduced by 50% in terms of increasing the substrate misorientation from nearly 0° to about 2.3°. In other words, the quality of GaN epilayer could be improved by using a SiC substrate with a larger misorientation. It should be noted that although the misorientation directions of substrates for samples C and E are different, the $I_y/I_b$ ratios of the two samples were nearly the same. That mean the $I_y/I_b$ ratio was not influenced by the misorientation direction.

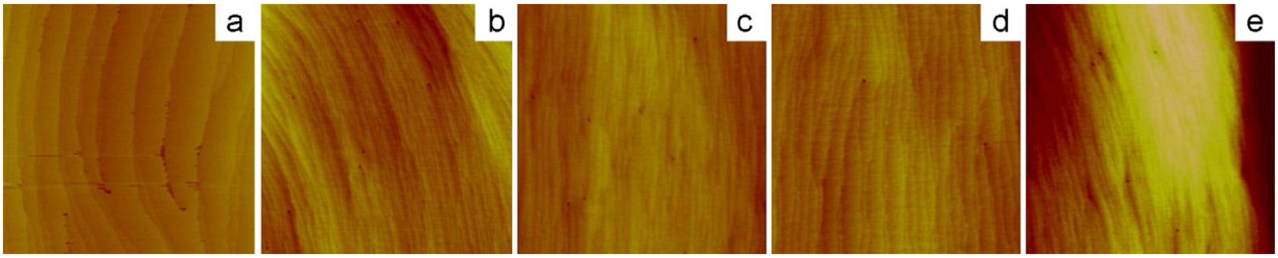

**Fig. 1.** AFM images of five samples. Images (a), (b), (c), (d) and (e) correspond to samples A, B, C, D and E, respectively. The AFM images were taken over an area of 2 μm × 2 μm.

**Table 2**
Dislocation densities of five samples after etching in molten eutectic of KOH–NaOH at 450 °C.

| | Density of screw dislocations (1/cm$^2$) | Density of edge dislocations (1/cm$^2$) |
|---|---|---|
| Sample A | $1.06 \times 10^9$ | $1.14 \times 10^9$ |
| Sample B | $6.38 \times 10^8$ | $7.33 \times 10^8$ |
| Sample C | $3.90 \times 10^8$ | $4.38 \times 10^8$ |
| Sample D | $5.33 \times 10^8$ | $4.10 \times 10^8$ |
| Sample E | $2.29 \times 10^8$ | $2.19 \times 10^8$ |

The densities of threading dislocations of GaN epilayer can be revealed by the etch pits in molten eutectic of KOH–NaOH [27,28]. In this work, the five samples were etched for 15 min in molten eutectic of KOH–NaOH at 450 °C.

After etching, the five samples were observed by SEM. Fig. 3 shows the SEM images of the five samples. In this figure, two types of etch pits with different sizes could be clearly identified. They corresponded to two types of dislocations. The lager pits were screw dislocations and the smaller pits were edge dislocations [29]. The densities of etching pits were calculated and listed in Table 2.

As shown in Fig. 3 and Table 2, sample A grown on on-axis substrate had the highest density of dislocations, including both the screw and edge dislocations. The density of dislocations of sample D grown on SiC substrate with a misorientation of 0.7° was reduced to about 1/2 of that of sample A. Furthermore the density of dislocations of sample E grown on SiC substrate with a misorientation of 2.3° was decreased to about 1/4 of that of sample A. This result implies that GaN epilayer grown on SiC substrate with a larger misorientation has a lower dislocations density. The same tendency could be found by checking the densities of dislocations in samples B and C. Now let us compare the densities of dislocations for samples C and E. For both samples, their substrates have same misorientation angle of 2.3°, but different misorientation directions. The density of dislocations of GaN epilayer grown on SiC substrate with a misorientation towards $[1\,1\,\bar{2}\,0]$ direction (sample C) is lower than that of GaN epilayer grown on SiC substrate with a misorientation towards $[1\,\bar{1}\,0\,0]$ direction (sample E).

It can be seen from our experiments, the dislocations density was reduced with the increase of the substrate misorientation. Most of dislocations in GaN epilayer were produced at the nucleation and initial growth stages. They originated from the coalescence of GaN islands which had reached a certain critical size during GaN growth [30]. If the GaN were epitaxial grown on a 6H–SiC substrate with a certain misorientation, the terraces steps would be limited by the misorientation of substrate. The initial growth of GaN includes two processes, i.e. island nucleation and atomic incorporation at the step edge. Bigger misorientation of substrate deduces the narrower terrace width. If epitaxial growth occurred on the substrate with a larger misorientation, the growth front from the step edges would soon coalesce with the nucleated islands before the islands reach the critical size, and then the density of dislocations in the epilayer were reduced. As mentioned in above paragraph, the density of dislocation of GaN epilayer grown on SiC substrate with a misorientation towards $[1\,1\,\bar{2}\,0]$ direction is lower than that of GaN epilayer grown on SiC substrate with a misorientation towards $[1\,\bar{1}\,0\,0]$ direction. This could be attributed to different terrace step widths of epilayer grown on SiC substrates with two different misorientation directions. The steps widths of sample C with a misorientation towards $[1\,1\,\bar{2}\,0]$ and sample E with a misorientation towards $[1\,0\,\bar{1}\,0]$ were measured to be 85 nm and 40 nm, respectively.

Fig. 4 shows the SEM images of samples A, B and C after etching in hot phosphoric acids at 200 °C. GaN in hot phosphoric acids has larger etching rate than in molten eutectic of KOH–NaOH [24]. In our experiment, the samples were intentionally over-etched in hot phosphoric acid. Therefore the density of etch pits in Fig. 4 could not stand for the actual density of dislocation; it was only used to characterize the erosion characters of the samples. There were two types of etch pits in Fig. 4 which exhibit white (W pits) and black (B pits) dots, respectively. Sample A had the largest number of B pits, but sample C had no B pits. This result implies that the density of B pits is reduced with the increase of the misorientation of substrate.

To distinguish the two types of pits, energy dispersive spectroscope (EDX) was used. Fig. 5 was a SEM image of a B pit, the chemical composition of point A in the black area was identified to be SiC by the EDX. It indicates that GaN epilayer in the black area has been completely etched up and the substrate has been exposed on the surface of the sample. Therefore, the GaN epilayer corresponding to the black area had a worse structural quality. In contrast, there are not any B pits in sample C, which means sample C has the best structural quality. Thus GaN epilayer grown on 6H–SiC substrate with bigger misorientation angle has better crystal quality.

FWHMs of symmetric 0 0 2 reflection and asymmetric 1 0 2 reflection rocking curves for samples A, D, and E are shown in Fig. 6.

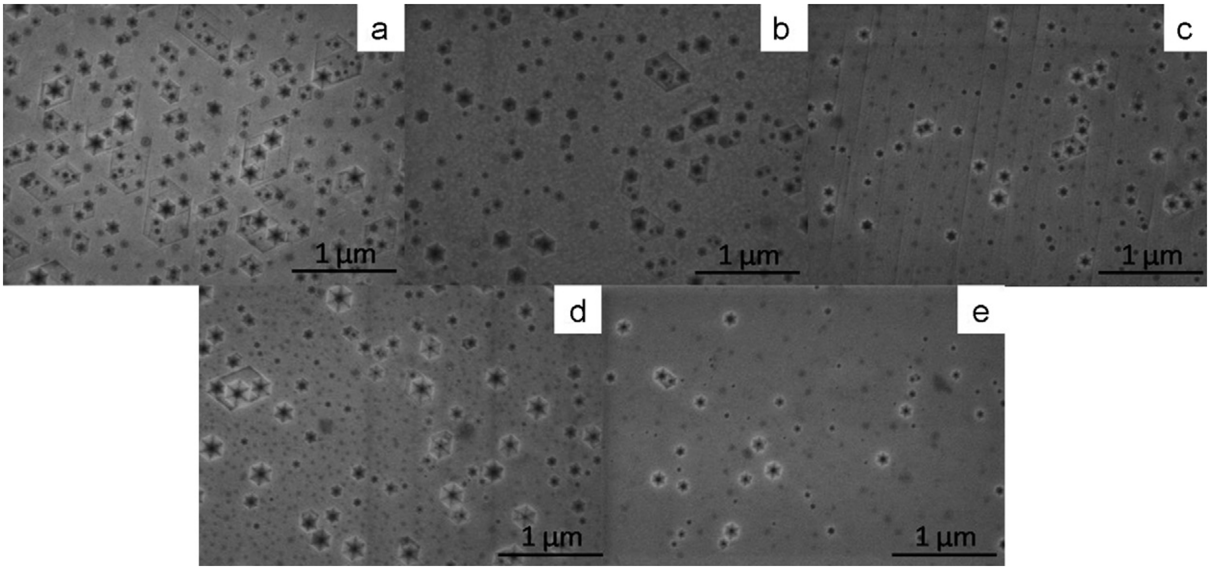

**Fig. 3.** SEM images of the five samples after etching in molten eutectic of KOH–NaOH at 450 °C. Images (a), (b), (c), (d) and (e) correspond to samples A, B, C, D and E, respectively.

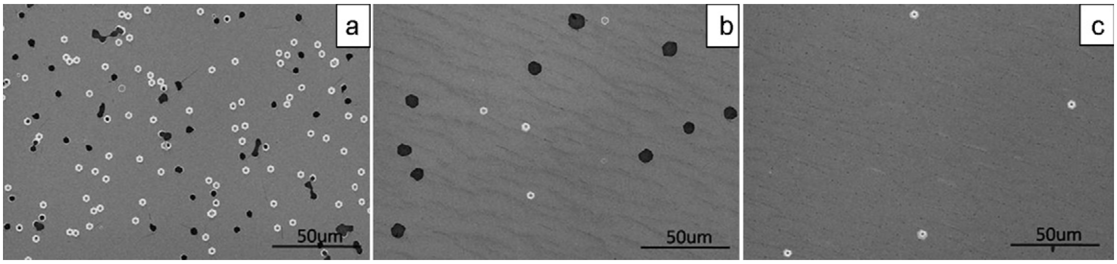

**Fig. 4.** SEM images of the samples after etching in hot phosphoric acid at 200 °C. Images (a), (b) and (c) correspond to samples A, B and C, respectively.

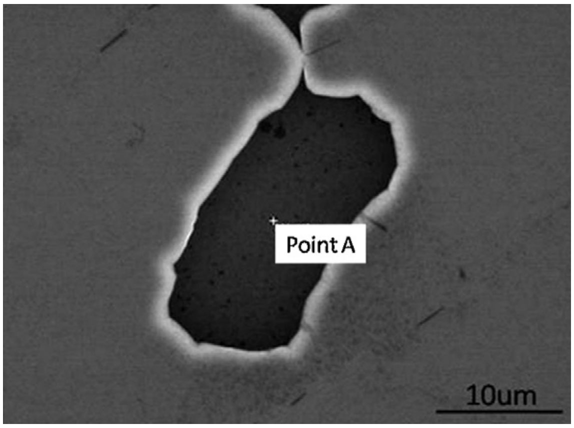

**Fig. 5.** SEM image of a black pit, an EDX analysis was performed at the point A.

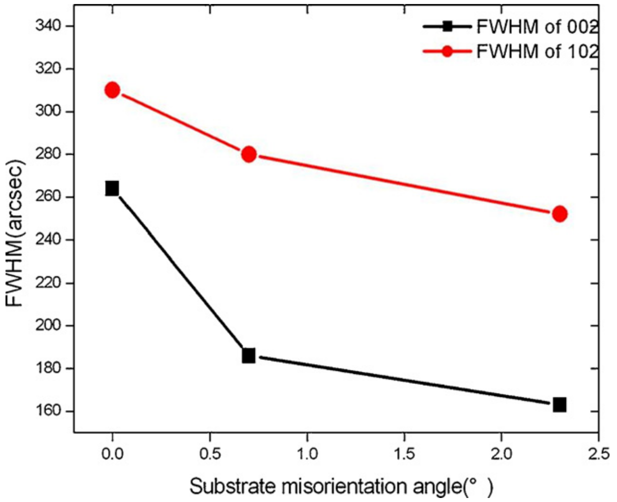

**Fig. 6.** The rocking curves of symmetric and asymmetric reflections for GaN epilayers grown on different SiC substrates. (●) and (■) correspond to the FWHMs of 1 0 2 reflection and 0 0 2 reflection, respectively.

The FWHMs of 0 0 2 and 1 0 2 reflection for the GaN epilayer grown on the on-axis SiC substrate are 264 and 310 arcs, respectively, whereas those for the GaN epilayer grown on the SiC substrate with a misorientation of 2.3° towards $[1\,1\,\bar{2}\,0]$ direction are reduced substantially to 163 and 252 arcs, respectively. That means the dislocations density can be reduced by using a substrate with a larger misorientation. The result is also confirmed by the observation of SEM.

## 4. Summary

In this work, the effect of misorientation of 6H–SiC substrate on the quality of GaN epilayer has been investigated. It was found that the atom step width, the $I_y/I_b$ ratio of the PL spectrum and the density of dislocations for GaN epilayer were significantly affected by the misorientation of 6H–SiC substrate. Larger misorientation of SiC substrate results in better crystal quality of GaN epilayer. The dislocations density was influenced not only by the misorientation angle but also by the misorientation direction, while the $I_y/I_b$ ratio of the PL was affected only by the misorientation angle. GaN epilayer grown on 6H–SiC substrate with a misorientation of 2.3° towards $[1\,1\,\bar{2}\,0]$ direction has the best crystal quality.

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