Revelation of dislocations in HVPE GaN single crystal by KOH etching with Na₂O₂ additive and cathodoluminescence mapping

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Abstract

Threading dislocations have been studied by means of etch pit method using molten KOH+Na₂O₂ solution, cathodoluminescence and transmission electron microscopy. We focus on the geometrical features of etch pits and their correlation with the recombination behavior at the dislocations. Four types of etch pits can be recognized after etching according to their sizes and depths, among which the middle-sized etch pits correspond to dislocations with the strongest non-radiative recombination. TEM observation has confirmed that dislocation beneath the large-sized etch pit is a mixed-type dislocation having both *c*- and *a*-component.

1. Introduction

Gallium nitride (wz-GaN) is one of the most promising wide bandgap semiconductor materials for the application of optoelectronic devices and power electronic devices that can work under high power density and at relatively high temperature. Due to the lack of high-quality bulky GaN crystal, GaN epi-films are typically grown on foreign substrates such as sapphire and SiC, and therefore contain high density of dislocations ($10^8 \sim 10^{10} \text{ cm}^{-2}$) due to large lattice mismatch [1]. This high density of dislocations seemed not fatal for the application of GaN-based light-emitting diodes (LEDs) that work at a low current density ($<40 \text{ A/cm}^2$) [2,3], however, for the application of Mega Watts power devices, laser diodes, or LEDs working at 1000 A/cm^2 or higher, much lower dislocation density is required.

Dislocations in GaN are mainly threading dislocations (TDs) that propagate nearly along the *c*-axis, unless in some cases they are intentionally bent towards the basal plane by substrate patterning for dislocation reduction. According to their Burgers vectors (*b*), TDs are generally categorized into edge-type (ED, *b*=*ma*), screw-type (SD, *b*=*nc*), and mixed-type (MD, *b*=*nc*+*ma*, *n*, *m*=1, 2 ..) dislocations. The different types of TDs may have different growth-related origins, and in real device applications they contribute differently to device degradation. Therefore, in the processes such as optimizing GaN growth condition and failure analysis of GaN devices, the ability to reveal the existence of dislocations and categorize them into different types is of great interest. Wet chemical etching (etch pit method) is a widely

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used technique for dislocation revelation in semiconductor materials since it is quick, easily accessible, and inexpensive, in addition to its low requirement for sample preparation. However, for GaN, the density, type and distribution of dislocations vary significantly due to growth-related conditions, which have posed several major problems for etch pit method: (1) severe pit overlapping and unclear pit shape for samples with dislocation density $> 10^8 \text{ cm}^{-2}$ [4]; (2) inconsistent correlation between etch pit geometry and dislocation types [5,6,7,8,9,10] for samples grown by different method; and (3) poor reproducibility and excessive dependence on sample condition.

In this work, we have applied molten KOH etching with Na_2O_2 additive (henceforth referred to as KN etching) to reveal and categorize TDs in HVPE GaN. By adding strong oxidizer Na_2O_2 , preferential chemical etching is enhanced [11]. As a result, etch pit geometries are more dependent on dislocation structure, rather than other factors such as the impurity element, doping level and growth method of the sample. In this way, reliable etch pit formation that can lead to a correct dislocation categorization of ED, SD and MD can be achieved. This has been confirmed in our previous research on GaN grown by different techniques, as well as on other wide band gap semiconductors such as 4H-SiC [11]. In this paper, we focus on HVPE GaN. Cathodoluminescence (CL) was applied to investigate the correlation between dislocation type and their electrical properties as carrier recombination centers. Transmission electron microscopy (TEM) observation was used to determine the Burgers vectors of dislocations.

2. Experimental

A 2-inch Ga-face GaN has been grown on sapphire substrate by halide vapor phase epitaxy (HVPE). The GaN growth layer separated itself from sapphire and became free-standing by natural stress-induced-separation [12]. CL spectra and mapping was performed before chemical etching in an SEM/CL system (JSM-7800) at room temperature. Accelerating voltage and beam current were 3 kV and 1 nA, respectively. Chemical etching in molten $\text{KOH}+\text{Na}_2\text{O}_2$ was carried out at temperature typically ranging from 400 to 600 °C for a duration of 5~30 min. Etch pit geometries have been observed by using a laser optical microscope or an SEM. Cross-section TEM sample has been fabricated by picking up a slab containing dislocation segment using focused ion beam (FIB). Weak beam dark field (WBDF) TEM observation was performed in a JEM-2010 working at 200 kV.

3. Results and Discussions

Fig. 1(a) shows a typical KN etched Ga-face. An advantage of KN etching over other etching methods like KOH/NaOH or $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ is that the etch rates at six facets of hexagonal pits are uniform and can be kept constant for a long time after the etching starts [11]. This allows us to achieve a desirable pit size by simply controlling the etch time. Four types of etch pits have been confirmed according to their geometrical features. Three of them are relatively deep and are grouped into large (L), middle (M), and small (S) -sized pits according to their $\langle 11\text{-}20 \rangle$ diagonal lengths. The

fourth type is called shallow (SH) etch pits in our work, which have clear pit cores at the center and similar lateral size as S-sized pits, as can be seen in the SEM image (Fig. 1(c)). But their six facets form much smaller angle with the c -plane than the other three types of etch pits. Information on pit size and density can be found in Fig. 1 and Table I.

Fig. 1 (a) Laser microscope image of etch pits formed on Ga-face of HVPE GaN by KN etching. Four types of etch pits have been confirmed. (b) CL panchromatic image of the same sample area. Note that CL image was taken before etching. (c) SEM image.

Table I. Sizes of L-, M- and S-sized etch pits and tentative attribution of dislocation types

Etch pit	L	M	S
Diagonal [11-20] size (μm)	1.34	0.86	0.46
Size normalized by “S”	2.9	1.8	1.0
Density (cm^{-2})	9×10^5	5×10^6	1×10^7
Possible disl. types	MD	SD	ED
Burgers vector, $\mathbf{b}$	$c+a$ (6.087 Å)	c (5.185 Å)	a (3.189 Å)
$ \mathbf{b} ^2$ (Å ²)	37	27	10
$ \mathbf{b} ^2$ normalized by “ED”	3.7	2.7	1.0

Fig. 1(b) shows the CL panchromatic image of the same sample area. Accelerating voltage of 3 kV resulted in an electron range around 100 nm from the sample surface. Dark spots in the CL image were caused by the existence of non-radiative centers, in this case dislocations. By comparing CL image with the etch pits, it has been found that CL dark spots have a one-to-one correlation with L-, M- or S-sized pit in terms of their positions. In comparison, at the positions of SH pits, no corresponding CL dark spots was found. These results indicate that dislocations that were related to L-, M- and S-sized pits are electrically active. They act as non-radiative recombination centers that trap carriers excited by the electron beam. A close look at the brightness (or darkness) of CL spots has revealed that those related to M-sized pits are darker than those of L- and S- pits, while the latter two are similar. The nature of SH pits is not clear so far. They could be caused by CL-inactive dislocations or they are related

to defects other than dislocations.

Table I compares the size and the density of L-, M- and S- pits. From our previous study [11], it was found that the ranking of [11-20] diagonal length of pits form by KN etching is consistent with the ranking of the magnitude of b . Since the pit sizes are clearly divided into three levels, it seems reasonable to correlate them with three simplest dislocation structures. Therefore, we tentatively attributed L-, M- and S-pits to MD with $b=c+a$, SD and ED, respectively. In addition, there is another reason of linking S-sized pits to TEDs: we found a dislocation array around the center (Fig. 1), on which etch pits are all of S-size. Similar phenomena have been confirmed in other areas of the 2 inch wafer. Dislocation arrays in a linear formation are typically related to EDs formed at the boundaries between different parts of the crystal.

Fig. 2 (a) CL spectra at room temperature. (b) Histogram of spot count as a function of the brightness at the dark spot center. (c) Relation between size of the dark spots and their brightness.

Fig. 2 presents a typical CL spectrum and the statistical analysis of the sample. The CL spectrum is featured with a strong and narrow near band edge (NBE) emission peak at wavelength $\lambda=363$ nm (3.42 eV) and a relatively weak and broad yellow band centered at $\lambda=550$ nm (2.25 eV), which is defect-related luminescence. Peak around $\lambda=726$ nm is caused by the second-order diffraction of the 363 nm peak. Position-dependent CL spectra taken at different types of dark spots did not shown any notable change in the spectrum shape at least within the wavelength range measured. The only effect seems to be the drop in the CL intensity, therefore, we believe that the dislocations in this sample are non-radiative recombination centers without characteristic luminescence. This is the reason we have chosen panchromatic CL mapping instead of monochromatic, to enhance the signal to noise ratio. Fig. 2(b) and (c) show the spot count and the size of the dark spots as a function of their brightness. The information has been extracted from an area about 10 times larger than Fig. 1. Note that only isolated dark spots that did not overlap with others have been taken into account. From the histogram in Fig. 2(b), dark spots can be divided into 3 groups by their brightness as three peaks are distinguished around 4000, 9000 and 11000. The first group with peak at 4000 is related to M-sized pits, and the other two peaks are related to L- and S-sized pits. Size of dark spots is defined as the number of image pixels with CL intensity lower than 50% of the dislocation-free

background. Brightness of dark spots is inversely proportional to their size, in agreement with the assumption that dislocations in this sample are non-radiative recombination centers.

Fig. 3 (a) SEM image before FIB sampling (b) Cross section FIB sampling for TEM observation

Fig. 3 shows the FIB process by which the cross-sectional TEM sample has been obtained. We first targeted an L-sized pit. The region containing the pit and the dislocation line beneath it was protected by a tungsten layer deposited on the surface, then the slab was picked-up after Ga-ion processing. Finally, the slab was thinned to a thickness of 150 nm for TEM observation. The V-shaped cross-section of the pit can be recognized in Fig. 3(b) and in TEM images of Fig. 4.

Fig. 4 TEM observation of the dislocation beneath an L-sized pit. (a) Bright field image with incident beam parallel to the $[1-100]$ direction; (b) BF image under two-beam condition with $g=0002$; (c) BF image under two-beam condition with $g=11-20$; (d) $g/3g$ WBDF image with $g=0002$; (e) $g/3g$ WBDF image with $g=11-20$.

Fig. 4(a)-(e) shows the results of TEM observation. Bright-field (BF) images with the incident beam parallel to the $[1-100]$ direction (Fig. 4(a)) and BF images under two-beam condition (Fig. 4(b) and (c)) clearly show the existence of dislocation segment extending from the core of etch pit. The length of the dislocation segment measured from the TEM image was about $1\ \mu\text{m}$, and its deeper end corresponds to the point where the dislocation crosses with the $\{1-100\}$ surface of the very thin TEM sample. $g/3g$ WBDF images taken under $g=0002$ and $g=11-20$ are shown in Fig. 4(d) and (e). It is well known that WBDF method provides better spatial resolution for the observation of crystal defects such as dislocations, as it emphasizes the contrast within a very small distance around the dislocation cores. The dislocation segment was on contrast in both images, suggesting the dislocation under the L-sized pit is a mixed-type dislocation having both the c - and a -component, which is consistent with our assumption shown in Table I. Further observation to determine the burgers vectors of dislocations under M-, S-sized pit and SH pit is on the way.

4. Conclusion

Etch pit method using molten $\text{KOH}+\text{Na}_2\text{O}_2$ solution was applied to HVPE GaN and it has revealed four types of etch pits: L-, M-, S-sized pits and shallow pit (SH). CL mapping showed that M-sized pits correspond to dislocations with the strongest non-radiative recombination, and L- and S-sized pits are weaker in comparison. Dislocation under SH pits (if any), are CL-inactive. TEM observation indicates L-sized pits are related to mixed-type dislocations, and determining $\mathbf{b}$'s for dislocations related to the other three types of etch pits is on the way.

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