Synchrotron radiation X-ray topography and defect selective etching analysis of threading dislocations in halide vapor phase epitaxy GaN crystal grown on ammonothermal seed

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Abstract

Halide vapor phase epitaxy GaN crystal is examined, in terms of threading dislocations, by two experimental techniques: synchrotron radiation X-ray topography and defect selective etching. The obtained results are analyzed and compared. Three kinds of threading dislocations are found. Other defects in the crystal are also shown. A correlation between defects determined by the two experimental methods is presented and discussed. © 2019 The Japan Society of Applied Physics

1. Introduction

Synchrotron radiation X-ray topography (SR-XRT) is a convenient and non-destructive characterization method suitable for materials with threading dislocation density lower than 105 cm−2.1,2 In SR-XRT, the continuous wavelength distribution of X-ray beam with very low divergence enables quick defect mapping on a large area. Additionally, SR-XRT is a technique extremely sensitive to strain and local lattice distortion caused by dislocations, which could be seen as diffraction contrast variation.3,4 Defect selective etching (DSE) is one of the most popular conventional methods for evaluation and characterization of etch pit density in a given area of crystalline material.5–7 Several different composition of etching mediums can be successfully used for revealing TD.8–10 The revealed etch pits can be correlated with types of threading dislocations.11–13 An analysis of threading dislocations by SR-XRT in GaN crystals grown by HVPE and ammonothermal14) methods was performed by Refs. 15–17 and Ref. 18. In both cases, only two types of dislocation contrasts were observed. They were correlated with threading screw dislocations (TSDs) and threading mixed dislocations (TMDs). No threading edge dislocations (TEDs) were found. The authors concluded that the TED density in ammonothermal GaN (Am-GaN) and HVPE GaN is extremely low. It was in opposite to the results of DSE of Am-GaN and Halide vapor phase epitaxy GaN (HVPE-GaN) presented by other authors, i.e.19–22 In these studies, three types of pits, in terms of their size, were distinguished on the c-plane of GaN: large, intermediate, and small. According to Ref. 23, they were correlated to TSDs, TMDs, and TEDs with densities 1 × 105 cm−2, 1–2 × 106 cm−2, and 5 × 106 cm−2, respectively.

In this paper defects in free-standing HVPE-GaN crystal, previously grown on Am-GaN and sliced from it,24) is analyzed by SR-XRT and DSE methods. Back reflection SR-XRT image contrasts of threading dislocations performed for the c-plane of HVPE-GaN are compared with images after DSE. A correlation between contrast of the SR-XRT spots and size of the etch pits is determined and described. It is shown that all three kinds of threading dislocations, screw, mixed as well as edge, can be detected by the SR-XRT method. Unfortunately, it is impossible to distinguish between TSDs and TMDs. However, all defects detected by SR-XRT are correlated one to one with the etch pits revealed by DSE.

2. Experimental methods

Figure 1(a) presents a GaN crystal sliced from free-standing HVPE-GaN grown before on an Am-GaN seed. The crystal growth technology and free-standing sample preparation were described elsewhere.24,25) The c-plane of the sample was prepared by lapping and chemo-mechanical polishing to an epi-ready state [see Fig. 1(b)].

The whole HVPE-GaN sample presented in Fig. 1(a) was mapped by SR-XRT. Back reflection topographs were recorded at the white beam TopoTomo beam line26) synchrotron radiation source ANKA at Karlsruhe Institute of Technology with particle energy 2.5 GeV on high resolution Slavich holographic films. Images were recorded with a sample-to-film distance of 80 mm and the sample tilted 8 deg about the horizontal axis perpendicular to the incident beam. Symmetric 0008 topographs were studied and the dominant wavelength in the 0008 topographs was 1.284 Å. In the back reflection geometry each diffracted beam forms a topograph image on the film. The image contains information on the defect structure in irradiated volume. In topograph images, high directed intensity (maximum fulfillment of diffraction conditions) is represented by dark color and low intensity (minimum fulfillment of diffraction condition) by white color.

After mapping the sample by SR-XRT, DSE in molten KOH–NaOH eutectic alloy was applied for revealing etch pits on the c-plane surface of the sample. The etching was carried out at 520°C. Images of the etched surface were performed with an optical microscopy with differential interference contrast and scanning electron microscope (SEM). The
pictures images (maps) from the SR-XRT and DSE were overlapped and compared.

3. Results and discussion

Figure 2(a) presents a full 0008 back reflection SR-XRT map of the HVPE-GaN sample. Well visible TDs walls and inclusions are marked. The inclusions are surrounded by curved basal plane dislocations (BPDs) and, in some cases, dislocation loops on pyramidal and/or prismatic glide planes. It is clearly seen in Fig. 2(b). For further analysis an area located far from the edge of the crystal was chosen. The area is marked as a white square in Fig. 2(a).

Figure 3 shows images from the white square area indicated in Fig. 2(a). Figure 3(a) presents the SR-XRT map. Black irregular lines as well as white and dark spots can be seen. The same area after DSE is shown if Fig. 3(b). Different kinds of pits, in terms of their size, are visible. Smaller parts of the examined area [marked as A and B in
Fig. 3. Images of the surface from the selected square area marked in Fig. 2(a) after (a) SR-XRT mapping; areas used for detailed comparison are marked as A and B; (b) DSE.

Fig. 4. Images of the sample surface from the areas A and B (white square) selected in Fig. 3 after: (a) and (c) SR-XRT; white spots—“w”, dark spots—“d”, BPDs pinned to the dark spots—“d*”; (b) and (d) DSE; large pit—“l”, intermediate pits—“m”, small pits—“s”.

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Fig. 3(a)] were chosen for a comparison between the results of SR-XRT and DSE. A relation between the spots from the SR-XRT map and the size of etch pits is presented in Fig.4 [area A in Figs. 4(a) and 4(b) and area B in Figs. 4(c) and 4(d)]. Figure 4(a) shows result of SR-XRT with three big white spots (marked as “w”) and several dark spots (marked as “d”). One of the white spots correlates to the largest pit in Fig.4(b) (marked as “l”). Two other spots are related to intermediate pits (marked as “m”). All dark spots overlap the smallest etch pits (marked as “s”). Additionally, in Figs. 4(a) and 4(c), few dark spots (marked as “d’”) are visible. The coincide with the BPD lines. A correlation of all spots determined by SR-XRT with all pits revealed by DSE is one to one. The density of white spots (large and medium etch pits) is lower than $3 \times 10^7 \text{ cm}^{-2}$. The density of dark spots (small etch pits) is of the order of $2 \times 10^4 \text{ cm}^{-2}$.

Figure 5 presents SEM images of three kinds of pits revealed in the sample by DSE. The sample was tilted by 45° for SEM imaging. It can be seen that the inclination of the side walls of large and medium pits [Figs. 5(a) and 5(b)] is greater than 45°. In turn, value of this angle is lower in case of the small pits [see Fig. 5(c)]. This result is in good agreement with work presented by Ref. 6. It was demonstrated, by AFM measurements of HVPE-GaN surface, that the inclination of the side walls of big pits is always higher than 45°. Additionally, using transmission electron microscopy as a calibration tool, it was shown that the largest pits are formed on screw, intermediate on mixed and the smallest ones on edge dislocations.6,14 Figure 6 shows that small etch pits are arranged in lines. This is characteristic for edge dislocations forming on areas of low-angle boundaries.17 Therefore, analyzing the pits presented in Fig. 5, one can suppose that three types of dislocations, screw, mixed and edge, were observed in the examined sample.

The visible pits have their equivalents in spots determined by SR-XRT. Big white spots represents TSDs and TMDs. Dark spots are correlated to TEDs. It is clearly shown in Fig. 4. It should be noted that a relatively large surface of the sample was analyzed: 750 × 750 μm (see Fig.3). However, the question how to distinguish screw and mixed dislocations by SR-XRT still remains. In the previous studies, Refs. 9,10 attributed the white spots to TSDs and the smaller black ones to TMDs. Ther e result presented in this work lead to an assumption that the contrast caused by the screw component seems to dominate the SR-XRT image. This contrast is the same for a mixed and a pure screw dislocation. Therefore, practically identical images in a symmetric 0008 XRT map are observed for these two types of defects in GaN. In theory, this applies only to the symmetric reflection, and the contrast of a screw and mixed dislocation should start to differ in an asymmetric reflection.27

In Fig. 3(a), besides white and dark spots, some black irregular lines are visible. The same black irregular lines are visible on Figs. 4(a) and 4(c). They correspond to BPDs. Moreover, some BPDs are pinned to TEDs which make the exact comparison difficult. Nevertheless one to one correlation between pits from DSE and spots from SR-XRT is possible. BPDs can be created due to the lattice mismatch between a new grown HVPE-GaN crystal and an Am-GaN seed. It should be kept in mind that there is a big difference in concentrations of impurities in HVPE and Am-GaN. Am-GaN crystals always contain $10^{18}–10^{19} \text{ cm}^{-3}$ of oxygen atoms as well as other impurities.28 In turn, the HVPE method allows to crystallize high purity GaN with extremely low level of unwanted elements.29,30 Therefore, the lattice mismatch between the two types of material leads to formation of strain and stress,31 then stress relaxation, and finally, BPDs. The BPDs are also shown in Fig. 2(a). They occurred in the area where inclusions were found. The inclusions were created by parasitic GaN particles which fell down on the crystal’s surface during the growth process. The presence of the inclusions in GaN structure can be a source of stress in grown layer and could lead to formation of the BPDs and dislocation loops. However, it was not the only reason for their formation. As mentioned, the sample [see Fig. 1(a)] was sliced from a
bigger HVPE-GaN crystal. The right side of the sample was close to the edge of the growing crystal. It is well known that one of the most significant problems of GaN crystallization in the c-direction (by any method) is simultaneous growth of GaN in the lateral directions. It was shown that the kind and concentration of impurities incorporated during the growth process on non-polar and semi-polar facets and on the c-plane are vastly different. This causes stress and finally can lead to plastic deformation of the deposited GaN layer. The stress starts from the edges of the growing crystal. Therefore, the BPDs and dislocation loops, visible in Fig. 2(a), could also be formed due to this phenomenon. In turn, the TDs walls, visible in Fig. 2(a), correspond to the not removed subsurface damage created during polishing of the sample.

The correspondence between large, intermediate and small pits with screw, mixed and edge dislocations, respectively, was presented in a few papers. In turn, Refs. 20, 21 reported that large pits were correlated with mixed type dislocations. A calibration of DSE with X-ray diffraction led to a conclusion that the large pits are formed on the screw dislocations while the small pits on mixed ones. Several factors can influence these inconsistent opinions. As was shown by Ref. 11, correlation of etching results with types of dislocations can vary for GaN grown by different methods. A different composition of etching mediums can also influence the kinetics of etch pit formation. This is a result of different type of purposely introduced doping elements and level of unintentional impurities in the material. As was discussed, both doping elements and impurities can be gathered along the dislocation lines and influence the nucleation and behavior of etch pits.

4. Conclusions

An analysis of threading dislocations by SR-XRT and DSE in free-standing HVPE-GaN grown before on an Am-GaN seed was presented. Back reflection SR-XRT image contrasts of threading dislocations for the c-plane of the sample were compared with images after DSE. Three kinds of threading dislocations, screw, mixed and edge, were detected by both methods. All defects were correlated one to one. For the first time, TEDs were correlated with features observed by SR-XRT. It was demonstrated that SR-XRT is a proper method for determining threading dislocations in GaN. Although, when a symmetric reflection is used for measurements, it is impossible to distinguish between TSDs and TMDs.

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Fig. 6. Images of the sample’s surface after DSE, three kinds of etch pits are visible.
