STUDY OF THIN FILMS POLARITY OF GROUP III NITRIDES

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Abstract

Thin films of GaN grown by MOCVD on (0001) sapphire were studied by transmission electron microscopy in order to correlate the observed extended defects with crystal polarity of the films. We propose relatively simple and unambiguous method of polarity determination for wurtzite group III nitrides based on the dependence of the intensity of diffracted beams upon thickness of the specimen. Due to the dynamic scattering by polar structure, the convergent beam electron diffraction patterns lose inversion symmetry and become in fact fingerprints of the structure carrying information about crystal polarity. In this study, we have used the thinnest regions of the specimens (< 15 nm) and multiple diffraction spots in high-symmetry orientation for polarity determination. The films were found to have Ga-polar surfaces, either being unipolar, or containing thin (10-30 nm in diameter) columnar inversion domains (IDs) of N-polarity. The occurrence of IDs was correlated with specific types of dislocation distribution in the films.

Introduction

In recent years the Group III nitride materials have generated tremendous interest due to their potential applications in high-efficiency LEDs (light-emitting diodes) and blue lasers. For device structures, high quality GaN and relative ternary alloy films and heterostructures are needed. The group III nitrides are materials with non-centrosymmetrical crystal structure, therefore, Ga- (Al-) polar or N-polar layers can be grown. Polarity of III-V nitride thin films is known to be an important factor in determining the surface roughness and properties of the as-grown material. Results of efforts of many groups on the polarity study are well reviewed by Hellman [1]. The primary focus of our investigations was the absolute polarity determination and correlations between the polarity and extended defects present in the GaN films grown on sapphire. The polarity of the layers was traditionally determined by convergent beam electron diffraction (CBED) [2-4] and multiple dark field transmission electron microscopy (TEM) techniques [5-6]. However, CBED method can only be applied for perfect crystals of considerable volume, while the GaN films often contain thin (of the order of 10 nm in diameter) pipe-like domains. The multiple dark field TEM imaging [5] allows to determine relative, not absolute polarity of such domains. Here we used a new method of polarity determination based on the different dependency of intensity vs. thickness for the specific diffracted beams revealing the non-centrosymmetric nature of the crystal. This allows the study of polarity for very thin, nanometer sized domains in GaN and other wurtzite structures as well as unambiguous absolute determination of film polarity.

Experimental

The GaN films in our study were grown on (0001) sapphire by metalorganic chemical vapor deposition (MOCVD) technique at temperatures around 1000^0 C. The details of the growth are reported elsewhere [7]. The films were found to be device-quality single-crystal and showed only excitonic bands in our photoluminescence studies [8]. Typical epitaxial relationships of $(0001)_{GaN} \parallel (0001)_{sap}$, and $[\bar{1}010]_{GaN} \parallel [\bar{1}\bar{1}20]_{sap}$ were observed for this system.

Multiple dark field technique was used to establish the inversion character of thin pipe-like domains observed in some samples. However, we were primarily interested in determining the absolute polarity of the layers and the inversion domains (IDs). For non-centrosymmetric crystal structures the opposite diffracted beams (those reflections of the diffraction pattern which reveal the non-centrosymmetry of the crystal structure) can have an order of magnitude difference in intensity due to dynamic (multiple) diffraction effects. Since the intensity of diffracted beams is also a function of a sample thickness, there is a unique distribution of intensity vs. thickness for each diffracted beam. The procedure to determine the absolute polarity of the films was to first calculate the intensities of different diffracted beams as a function of crystal thickness by multislice calculations. Experimental CBED patterns of different regions of GaN films in $[1\bar{2}10]$ orientation were obtained using small (about 2-4 nm) probe size. To determine the absolute polarity, we had to estimate the thickness of the crystal for the region of the CBED patterns to make sure that the thickness was below the critical for unambiguous results value. For that, the high resolution TEM (HRTEM) images were taken along with CBEDs and then compared with the simulated high resolution images obtained for wurtzite GaN. The multislice calculations for wurtzite GaN crystal structure in $[1\bar{2}10]_{GaN}$ zone were done using MacTempas© software. We also introduced into the calculations small (up to 1 mrad) tilts of the entire unit cell about the $[1\bar{2}10]_{GaN}$ direction. This corresponds to the tilt observed in most of the experimentally obtained TEM images of group III nitride films. The details of the image simulations in conjunction with polarity determination of wurtzite structures are reported elsewhere [9]. Experimental high-resolution TEM images and convergent beam diffraction patterns of GaN layers were obtained using Topcon 002B (200 kV) electron microscope with standard LaB_6 filament. The microscope has point-to-point resolution of 1.8 Å and nano-probe size beam capabilities.

Results and Discussion

According to our previous results [8, 10] two types of microstructure were found to be characteristic of MOCVD grown GaN films. Density of about 10^9 cm^{-2} was found to be typical for all extended defects (inversion domain boundaries, pure edge, mixed and screw dislocations) present in the films of the first type (A). The films of the second type (B) were found to be free from inversion domains and with low (down to 10^7 cm^{-2}) density of screw and mixed type dislocations. Here low-angle tilt sub-grain boundaries and associated with them threading edge dislocations (density ~ 10^{10} cm^{-2}) were found to be the main defects.

Fig. 1 (a) shows the typical cross-sectional TEM image of an A-type GaN film grown on basal plane of sapphire. The image was taken under $\vec{g}$=0002 weak beam dark field conditions near the $[1\bar{2}10]_{GaN}$ zone. It clearly shows the ~ 10 nm size columnar domain (marked by an arrow). From the cross-sectional TEM micrographs, the density of these pipe-type domains was calculated to be about 10^9 cm^{-2}. We carried out multiple dark field TEM studies of these domains [10]. They showed inversion of the contrast in the images formed under the 0002_{matrix} and $000\bar{2}_{matrix}$ reflections (near the $[1\bar{2}10]_{GaN}$ zone) which established them to be domains of the opposite with respect to the matrix polarity. To determine the absolute polarity of the ID and the matrix material, we carried out calculations of intensities of different diffraction beams for the $[1\bar{2}10]$ zone of GaN wurtzite crystal structure as a function of specimen thickness. In our calculations, we assumed that the positive [0001] direction of the structure corresponds to the Ga-N bond as it is shown in the

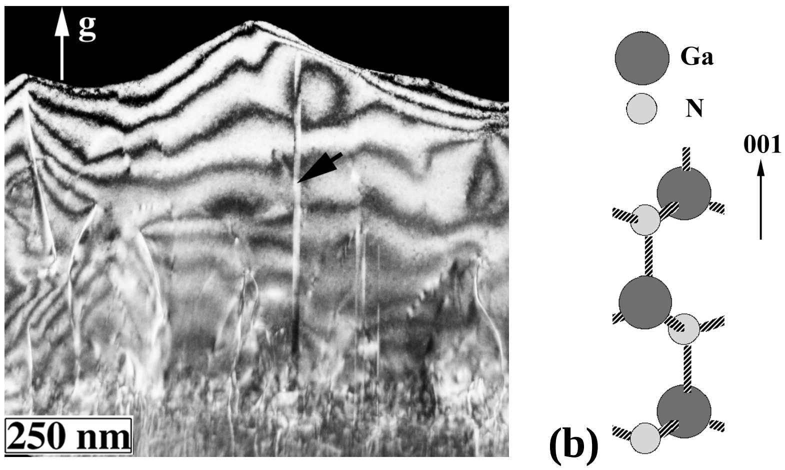
(a) 

Fig. 1
(a) Weak beam dark field cross-sectional TEM image of a GaN film grown on sapphire. The arrow indicates the inversion domain. The image is taken near the $[11\bar{2}0]_{GaN}$ zone.

(b) Schematic representation of a GaN crystal structure viewed in $[11\bar{2}0]$ direction.

schematic representation of the GaN crystal structure in the Fig. 1 (b). The plots in Fig. 2 (a, b) show the calculated intensity vs. crystal thickness for 0002 and $10\bar{1}1$ GaN beams, respectively. The calculations were done for the reflections belonging to the $[1\bar{2}10]$ zone of GaN, no tilt was introduced into the calculations. The intensity of 0002 reflection for sample thickness in the range of 100 Å is about an order of magnitude higher than that of the opposite $000\bar{2}$ beam (Fig 2 a). For the other reflection (Fig. 2 (b)), there is again an order of magnitude difference in intensity between $[10\bar{1}\bar{1}]$ and $[10\bar{1}1]$ beams, the former being stronger in regions about 100 Å thick, the latter being stronger for about 200 Å sample thickness. Similar plots were calculated for different diffracted beams of the GaN $[1\bar{2}10]$ zone with and with out introduction of $\leq$1 mrad tilt. Hence, for the thinnest (below 140 Å) regions of GaN we expect to obtain higher intensity of 0002 CBED disc as compared to the opposite $000\bar{2}$.

We studied the polarity of many device-quality films grown by MOCVD and it was found that the layers had Ga-polarity (according to schematic representation shown in the Fig. 1 (b)). In each case, we took the HRTEM images along with the CBEDs in order to determine the thickness of the sample and made sure that it was below the thickness (~ 140 Å) where dynamic diffraction could give confusing results. As we have previously found, the samples containing IDs have Ga-face polarity. The CBED patterns and HRTEM images were obtained for adjacent areas inside and outside of the pipe-like domains. The results of our study are presented in Fig. 3. The small probe (about 3 nm in diameter) was used to obtain CBEDs outside (Fig. 3, a) and inside (Fig. 3, b) of

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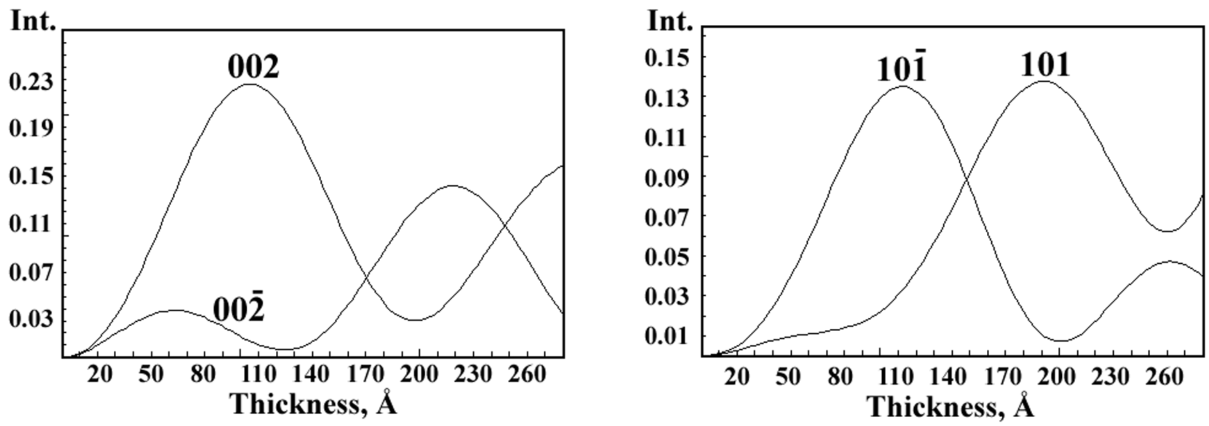

Fig. 2. Calculated intensities (arbitrary units) of <0002> and $<10\bar{1}1>$ beams vs. sample thickness (Å) for $[1\bar{2}10]$ zone of wurtzite GaN crystal structure.

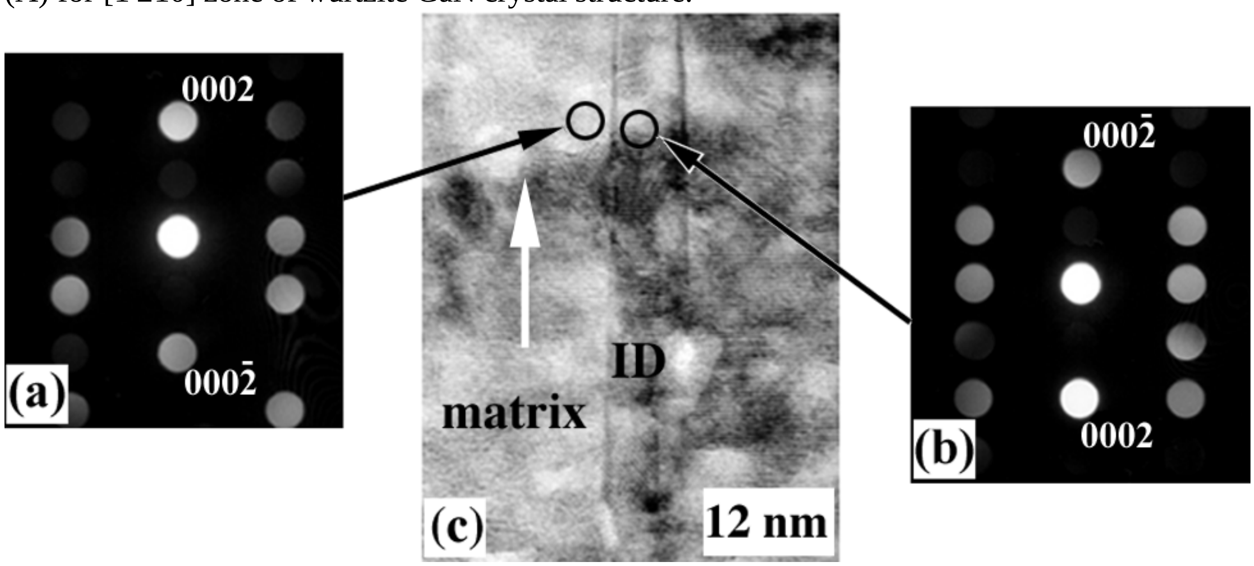

Fig. 3. CBED patterns obtained from (a) the GaN matrix; and (b) the inversion domain ID. The TEM image of the corresponding area of the cross-sectional GaN sample is shown in (c). Positions of the electron beam for taking the CBEDs are shown by circles. White arrow indicates the direction of film growth.

the inversion domain shown in Fig. 3 (c). The intensity of one <0002> type CBED disk in matrix diffraction pattern is much higher than that of the opposite disk. The comparison of the experimental HRTEM images taken in this particular place of the sample with results of our simulations [9] allowed us to estimate the thickness of the GaN layer to be about 70-90 Å. From the graph in Fig. 2 (a) for this thickness region, we can see that the intensity of 0002 beam is much stronger than that of $000\bar{2}$. The intensity of $10\bar{1}\bar{1}$ beam from Fig. 2 (b) is much higher then the intensity of $10\bar{1}1$ beam. The distribution of intensities of CBED discs in Fig. 3 (a) confirms that the positive $[0002]_{matrix}$ direction of GaN matrix is directed along the growth axis of the film (indicated by a white arrow in Fig. 3 (c)). The CBED pattern taken inside the ID shows that the positive $[0002]_{ID}$ direction is opposite to the axis of growth. The simulated CBED pattern with indexed reflections calculated for the GaN thickness of 80 Å is shown in Fig. 4, which is in a good agreement with the experimental result (Fig. 3 (a)). It should be noted, that the effect of small tilt (within 1 mrad) can produce slight variation in distribution of intensities of CBED disks. Nevertheless, general tendencies in the intensity vs. thickness curves remain the same. The study was repeated on many IDs found in several GaN films.

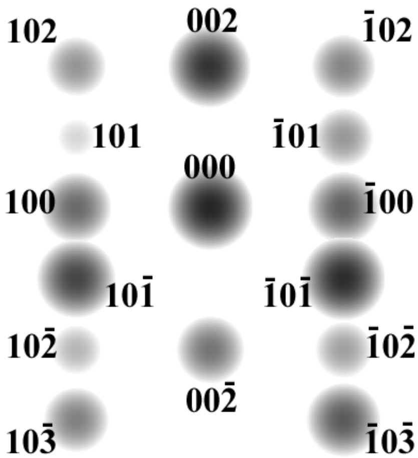

Fig. 4. Simulated convergent beam electron diffraction pattern obtained for 80 Å thickness of the $[1\bar{2}10]$ zone of GaN wurtzite structure. The reflections are indexed.

In accordance with our previous studies [8, 10] in unipolar (Ga-polar) films the major defects were found to be edge dislocations with the Burgers vector $\vec{b}=1/3[11\bar{2}0]$ primarily associated with low angle tilt sub-boundaries. No inversion domains were observed in these layers. The different type of microstructure is correlated with the presence of inversion domains of N-polarity. These films were found [10] to have approximately same density (about 10^9 cm^{-2}) of all extended defects present in the layers such as: screw, mixed and edge dislocations, IDs and basal stacking faults. We have also studied the influence of the layer polarity on surface roughness and to establish the relative rates of growth for different polarities. There are observations of flat and rough (grainy) surfaces in the case of Ga-polar GaN films containing no IDs, and pyramidal-type surfaces for N-polar GaN films [11]. Based on the experimental observations, the N-polar GaN surface was suggested to grow slower than the Ga-polar one [11]. This could also explain the observation of nanotubes in III-V materials as N-polar domains grow slower than the surrounding Ga-polar matrix and after certain thickness leaves empty tubes [4, 12, 13]. However, in our study, films were observed to be of Ga-polarity containing N-polar IDs. The surface of these ID-containing films was observed to be either rough with gaps and hillocks up to 200 nm or smooth within 2 nm range depending upon the growth conditions [10]. Rough GaN films mostly showed the presence of N-polar inversion domain just in the middle of a hillock. In the smooth ID-containing films, the IDs were threading through the whole layer thickness ending at the top surface. Thus, from our observations we can conclude that the dependence of the growth rate vs. surface polarity of GaN can itself be a function of growth conditions such as growth temperature and III/V flux ratio.

Conclusions

We have established the predominance of the Ga-polarity studying device-quality MOCVD films. The films are either unipolar, or contain thin N-polar pipe-like domains with the diameter of 10 - 30 nm. The polarity of thin areas of the III-V nitride samples has been determined by studying the distribution of intensities of the diffraction in high-symmetry CBED patterns. The CBED patterns lose inversion symmetry due to dynamic scattering and become in fact fingerprints of the structure carrying information about crystal polarity. The thickness of the sample can be estimated by comparing the experimental HRTEM images taken at the same places as CBEDs

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with results of multislice image simulations. The polarity of the layers was correlated with the surface roughness. The Ga-face polar films containing IDs showed high (about 10^9 cm^{-2}) density of edge as well as screw dislocations randomly distributed throughout the layer, while the unipolar (Ga-polar) films had predominantly b=1/3[$11\bar{2}0$] dislocations (of about 10^{10} cm^{-2} density) associated with low-angle tilt sub-grain boundaries. Finally, from our observations of Ga-polar films with inclusions of IDs having both smooth (± 2 nm) and rough (± 200 nm) surfaces, we envisage that the ratio of growth rates of different polarities in Group III nitride films depends upon the growth conditions determining the overall film growth velocity.

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