M R S Internet Journal of Nitride Semiconductor Research

Volume 1, Article 33

Correlation between surface morphologies and crystallographic structures of GaN layers grown by MOCVD on sapphire

J. L. Rouviere, M. Arlery
CEA/Grenoble, Département de Recherche Fondamentale sur la Matière Condensée/SP2M

R. Niebuhr, K. H. Bachem
Fraunhofer Institut für Angewandte Festkörperphysik

Olivier Briot
Groupe d'Etude des Semiconducteurs, GES-CNRS

This article was received on June 20, 1996 and accepted on November 5, 1996.

Abstract

GaN layers deposited by MOCVD on sapphire have been characterized by Transmission Electron Microscopy (TEM). Two substrate orientations were used, (0 0 0 1) and$(2\ \bar{1}\ \bar{1}\ 0)$.We determine the crystallographic structures (defect content and layer polarity) of three different types of GaN layers with different surface morphologies. Convergent Beam Electron Diffraction studies were particularly important to determine the polarity of the GaN layers. We find that polarity and surface diffusion are the factors that control the different growth modes. Unipolarity is obtained thanks to the annealing of the low temperature buffer layer or/and thanks to the nitridation of the sapphire substrate.

Hexagonal pyramids and flat tops are formed when the material has a dominant N-polarity. The pyramids contain many tiny hexagonal columnar Inversion Domains (IDs). These pyramids are formed when the tiny Ga-polar IDs grow faster than the surrounding N-polar matrix. Flat GaN layers are unipolar, with a Ga polarity. Rough grainy layers which are unipolar (Ga-polarity) are obtained when surface diffusion is not high enough.

1. Introduction

With the realization of gallium nitride diodes and more recently laser diodes [1], GaN has attracted much attention and there is now little doubt that GaN will be an important semiconductor in optoelectronic applications. Although all the major semiconductor devices have now been realized, the material is far from being mastered and many challenging problems still remain.

The long-standing problem of GaN growth is the lack of a suitably adapted substrate. (0001) sapphire plane is the most popular and most successful substrate in spite of its huge lattice mismatch with GaN (-13%). Many alternative substrates have been tested [2]. The success of GaN growth on sapphire comes from the use of a low temperature buffer layer [3], but the exact role of this buffer layer has not yet been determined. It has recently appeared that the nitridation of the sapphire substrate could be as important as the buffer layer itself [4] [5] [6].

In this communication, we report Transmission Electron Microscopy on MOCVD grown GaN layers on (0 0 0 1) sapphire. We determine the crystallographic quality of different GaN layers with different surface morphology. We then determine the factor that controls the different growth modes. These results could help in improving further the GaN film structure.

2. Experimental details

Most of the samples we have observed were grown in an AIXTRON 200 MOCVD apparatus [7]. A=(2 1 1 0) and C=(0 0 0 1) sapphire substrate planes were used. Different buffer layers (GaN or AlN) were tested with different degrees of nitridation. In addition to these samples, we observed a sample grown in an ASM OMR 12 MOCVD apparatus, on a nitrided (0 0 0 1) sapphire plane [5].

Specimens for TEM were prepared using the standard techniques : mechanical polishing and Argon ion milling. TEM observations were realized on a JEOL4000EX electron microscope (Scherzer resolution about 0.17nm) which was used for both High Resolution Electron Microscopy (HREM) and conventional TEM observations. Convergent Beam Electron Diffraction experiments to determine the polarity of the layers were realized on a JEOL3010 electron microscope [8]. On–axis CBED patterns were realized along a <0 1 $\bar{1}$ 0> direction.

3. Experimental results

GaN is difficult to grow. One of the first goals of the grower is to obtain an optically flat, mirror–like GaN surface. By observing the surface morphology of the GaN layer, the quality of the growth can be determined. We have characterized the three kinds of GaN films (see figure 1) that growers generally observe according to different growth conditions:

- (a)Rough GaN layers containing hexagonal pyramid and plateaus
- (b)GaN layers having a flat or nearly flat surface
- (c)GaN films having a rough grainy surface.

Table I summarizes the conditions under which sample types (a), (b) and (c) can be obtained. The type (a) sample is obtained when no special care is taken concerning the buffer layer (for instance no special annealing of this buffer layer as in table I or a complete absence of this buffer layer).

We present and discuss each type of layer in turn.

3.1. GaN layers with hexagonal pyramids and flat tops

Although both flat tops (that is to say plateaus) and pyramids might occur in the same sample, we regard the occurrence of the pyramids as the essential observation that defines this type of film morphology.

We now understand the structure of these pyramids. TEM observations reveal that the pyramids contain both planar and linear (dislocations) defects. Convergent Beam Electron Diffraction experiments have proved that these planar defects are Inversion Domain Boundaries (IDBs) on the {0 1 $\bar{1}$ 0} planes (see figure 2) . Six IDB planes enclose a single Inversion Domains (IDs) and define the characteristic hexagonal columnar shape of this IDs. The hexagonal shape is best seen on a plan view image of the samples (see figure 3). In a low magnification TEM image of a [2 $\bar{1}$ $\bar{1}$ 0] cross-section (see figure 2) only the projection of two parallel IDBs (out of six) can be seen. The ID, which is in between these two vertical lines, starts at the buffer-layer/over-layer interface and extends directly towards the surface. The determination of the relative polarity of the two domains follows straightforwardly from the observation of the rotation of the CBED pattern when the electron is moved into an ID. The determination of the absolute polarity is more difficult: calibrations of the microscope and of the CBED simulations are necessary. We have done such calibrations and find that the matrix is N-polar and that the IDs are Ga-polar (see figure 2 for the definition of polarity) [9]. We attribute the pyramid shape to a different growth rate between the two polarities. The Ga-polar domains grow faster than the surrounding N-polar matrix. A pyramid contains many IDs. An ID is always observed at the apex of the pyramids, the other IDs are generally located at the steps on the GaN surface (see figure 2).

We have some interesting information on hexagonal flat tops, which can be considered to be truncated pyramids. TEM cross-section and plan view reveal that flat tops do not contain IDBs (see figure 4). CBED experiment has shown that the hexagonal flat tops adjacent to pyramids have a N-polarity.

In summary, pyramids are the signature of the presence of tiny IDs (with a Ga polarity) in a GaN layer which has a N-polar matrix.

3.2. Flat GaN films

All of the flat or nearly flat GaN layers (that is to say GaN layers with a few grooves, see figure 6b) that we have observed are unipolar with the Ga-polarity. As CBED calibrations are rather tricky, we have double checked our absolute polarity determination by an ion-channeling technique [9]. Our observations show that the selection of the Ga polarity can be achieved when special care is taken in the growth of the low temperature buffer layer. All the buffer layers contain a high density of defects (about $10^{12}/\mathrm{cm}^2$) (figure 5,figure 6). This high density makes a complete characterization difficult, but most of them look like dislocations joining columnar grains. A few stacking faults (or Inversion Domains ?) on the c-plane and sometimes on the $(1\,\bar{1}\,0\,1)$ planes could also be observed (see figure 5). Surprisingly, the flatter layers we have observed contain vertical defects located near the buffer layer. These vertical defects do not propagate throughout the layer. From HREM pictures, some of these planar defects look like the Inversion Domains of the “pyramidal samples», but this should be verified with CBED experiments (see figure 5). The non-propagation through the layer of the few IDs could easily be explained by the different growth velocity of two phases: the N-polar domains growing slower than the adjacent Ga-matrix would be swallowed during the growth. This different growth rate between the two polarities could also contribute to the formation of the nanopipes that have been frequently reported [10], as a few of the N-polar domains could remain open and reach the surface. As rougher samples (see next sections) have been observed without any IDs, the presence of these IDs in these flat samples seems to indicate that the selection of polarity, which apparently occurs during the crystallization of the buffer layer, has not been optimized and could be improved. Recent results have shown that the optimized nitridation of the sapphire could improve the optical properties of the layers [6]. The exact role of this nitridation is still unclear but it could help in selecting the unipolar material.

3.3. Rough grainy surface GaN films

Rough grainy films are entirely unipolar, with a Ga-polarity. These layers contain only dislocations that are located at the intersection of the grains. The surface has a tendency to be faceted on the $\{1\,0\,\bar{1}\,1\}$ planes. By increasing the growth temperature from 900°C to 950°C a nearly flat surface (type b) was obtained that from time to time contained a groove with $\{1\,0\,\bar{1}\,1\}$ facets (see figure 6). We thus attribute the roughness of these films to too low a surface diffusion during the growth.

Several layers were systematically grown on **A**=$(2\,\bar{1}\,\bar{1}\,0)$ and **C**=(0 0 0 1) sapphire planes and we find the same kind of behavior for the two substrate orientations (see table I). This indicates that the surface morphologies we have observed do not depend too much on the substrate, but are characteristics of the GaN layer itself.

As far as the surface morphology is concerned, there is not much difference between a surface containing only hexagonal flat tops (a case we have not observed but is often reported in literature) and a flat surface presenting occasional hexagonal grooves (case (b), see figure 6b). One can however see a difference in surface coverage: the hexagonal plateaus coalesce to form a flat surface with a few grooves in between. We incline to regard these kinds of samples as Ga-polar samples. On the other hand, hexagonal flat tops associated with pyramids are generally less uniform in height and are generally clearly isolated from each other and we tend to regard these kinds of samples as N-polar samples. However, determining the polarity of the material just by its surface appearance is not yet reliable. More polarity work needs to be done on samples having a hexagonal flat top appearance with no pyramids at all.

Our observations tend to indicate that the N-polar material (case a) is more difficult to grow than the Ga-polar material (case b-c). It is clear that the polarity problem has been greatly overlooked in GaN : selecting the right polarity (the Ga-polarity) is the first step to overcome in GaN growth. Polarity could be also responsible for the different luminescence of different domains of non uniform GaN layers [11] : IDBs and N-polar materials might contain point defects which could be optically active.

4. Conclusion

We have characterized GaN films grown by MOCVD on (0 0 0 1) and $(2\,\bar{1}\,\bar{1}\,0)$ sapphire planes by TEM, and determined the exact crystallographic structure of three types of GaN films displaying different surface morphologies. Polarity and surface diffusion are the important factors that determine the surface morphology. Flat layers are obtained when the surface diffusion is high enough and the material is unipolar with a Ga polarity. Hexagonal pyramids and flat tops are formed when the material has a dominant N-polarity. The pyramidal growth occurs when the N-polarity is not complete: tiny Ga-polar domains growing faster than the N-polar matrix steer the growth and create pyramids. A rough grainy surface can be obtained with a unipolar Ga-polar layer when the surface diffusion is two low. These observations have emphasized that the correct way to get rid of the IDs involves the crystallization of the buffer layer or/and the nitridation of the sapphire substrate.

Acknowledgments

Part of this work has been supported by the EU commission under the Brite-Euram II program (Project BE-7036, BRE2-93-0526). We thank Dr. U. Kaufmann, the coordinator of this European project. We thank Dr A. Bourret and Dr B. Daudin for helpful discussions.

References

[1] Shuji Nakamura, Masayuki Senoh, Shin-ichi Nagahama, Naruhito Iwasa, Takao Yamada, ToshioMatsushita, Hiroyuki Kiyoku, Yasunobu Sugimoto , *Appl. Phys. Lett.* ***68***, 2105-2107 (1996).

[2] E. S. Hellman, C. D. Brandle, L. F. Schneemeyer, D. Wiesmann, I. Brener, T. Siegrist, G. W. Berkstresser, D. N. E. Buchanan, E. H. Hartford, Jr., *MRS Internet J. Nitride Semicond. Res.* ***1***, 1 (1996).

[3] I. Akasaki, H. Amano, Y. Koide, K. Hiramatsu, N. Sawaki, *J. Cryst. Growth* ***98***, 209 (1989).

[4] Akio Yamamoto, Mitsunori Tsjino, Mitsugu Ohkubo, Akihiro Hashimoto, *J. Cryst. Growth* ***137***, 415-420 (1994).

[5] O. Briot, J. P. Alexis, B. Gil, R. L. Aulombard, *Mater. Res. Soc. Symp. Proc.* ***395***, 207-212 (1996).

[6] O. Briot, J. P. Alexis, B. Gil, R. L. Aulombard, unpublished (1996).

[7] R. Niebuhr, unpublished (1996).

[8] J. -L. Rouviere, M. Arlery, A. Bourret, R. Niebuhr, K. -H. Bachem, *Mater. Res. Soc. Symp. Proc.* ***395***, 393 (1996).

[9] B Daudin, JL Rouviere, M Arlery, *Appl. Phys. Lett.* ***69***, 2480-2482 (1996).

[10] W Qian, M Skowronski, K Doverspike, LB Rowland, DK Gaskill, *J. Cryst. Growth* ***151***, 396 (1995).

[11] C. Trager-Cowan, K. P. O'Donnell , S. E. Hooper, C. T. Foxon , *Appl. Phys. Lett.* ***68***, 355-357 (1996).

Table I

Preparation conditions and main characteristics of six different samples grown on A and C-sapphire planes that are representative of the three types (a,b or c) of samples

Surface morphology	(a) Pyramids	(b) Flat or nearly flat	(c) Grainy
Sapphire orientations	A and C	A and C	A and C
Buffer layer	GaN 600°C	AlN 800°C	AlN 800°C
	not annealed	annealed at 1000°C	annealed at 1000°C
GaN Layer	GaN 1150°C	GaN 950°C	GaN 900°C
Polarity and ID	N-polar matrix with IDs	Ga unipolar no IDs	Ga unipolar no IDs
	see figure 1a	see figure 1b, figure 5b	see figure 1c

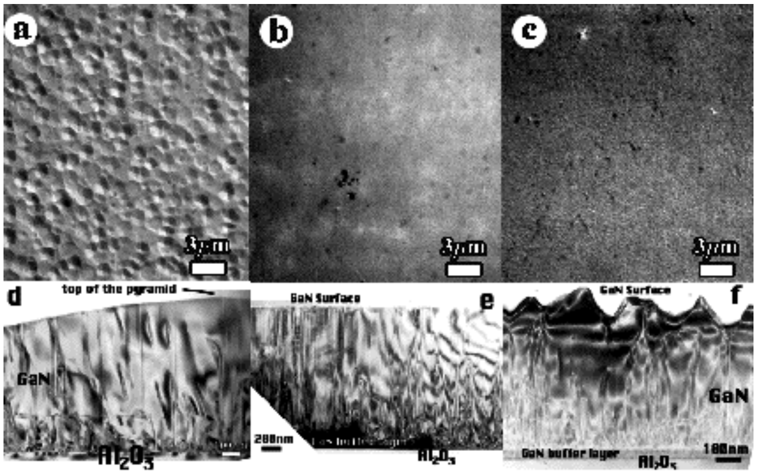

Figure 1. Optical images (a,b,c) and TEM cross-sections (d,e,f) of the three types of GaN layers grown on c-sapphire substrate. (a,d) GaN layer with hexagonal pyramids and hexagonal flat top at its surface: the material is mainly N-polar (see figure 2) (b,e) Flat GaN layer. The material have a Ga-polarity. Far from the buffer layer, only dislocations are present. (c,f) Rough grainy surface. This material has a Ga-polarity and contains only dislocations. The surfaces have $\{0\ 1\ \bar{1}\ 0\}$ facets.

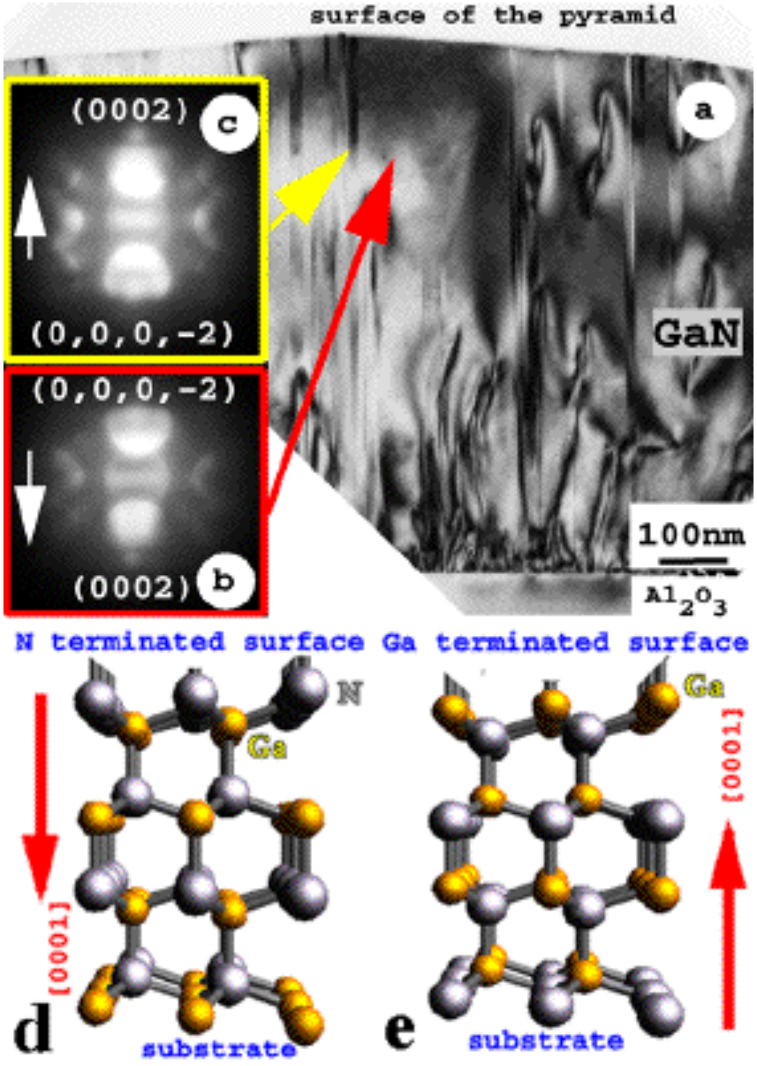

Figure 2. Polarity of GaN (a) TEM cross-section of a pyramidal step. An Inversion Domain is situated at the apex of the pyramid. (b,c) $[0\ 1\ \bar{1}\ 0]$ on-axis CBED patterns respectively taken inside (c) and outside (d) the vertical strips. As the patterns are rotated 180° from each other the vertical strips are Inversion Domains. CBED calibrations indicate that the tiny hexagonal columns have a Ga-polarity and that the matrix has a N-polarity. (d-e) Crystal structure viewed along the $[2\ \bar{1}\ \bar{1}\ 0]$ direction used to simulate the CBED patterns. The positive c-direction is defined by the vertical Ga-N bonds: c starts on the Ga atom and points to the N atom. The material is said to be Ga-polar (c,e) (respectively N-polar (b,d)) when c points out from (respectively into) the GaN layer. The "natural» surface is then Ga-terminated (respectively N-terminated).

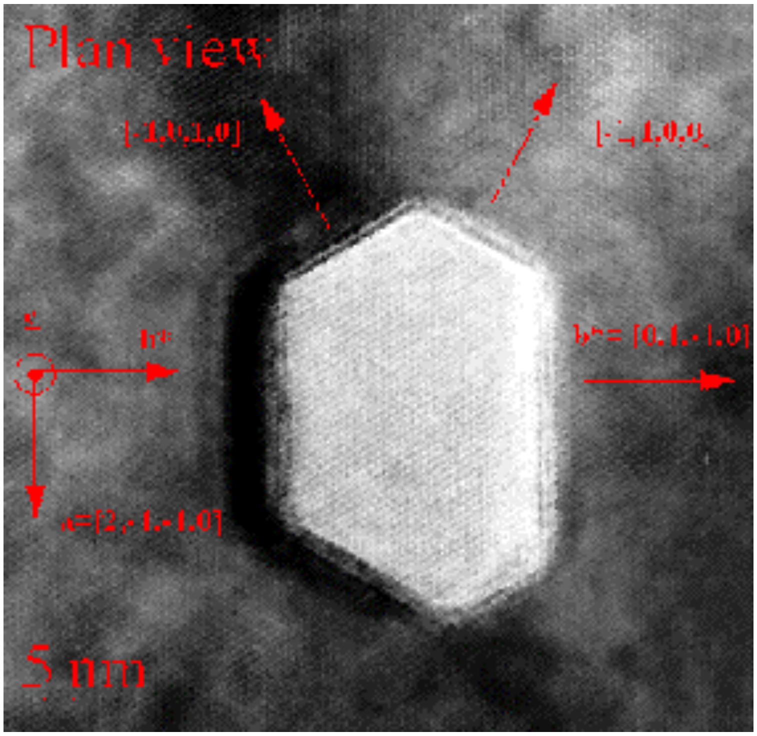

Figure 3. Plan view image (direction of observation : [0 0 0 1]) of a GaN layer showing the hexagonal shape of the columnar Inversion Domains. The inside of the hexagon is not empty of GaN material; it contains a Ga-polar GaN material. The ID is brighter than the surrounding matrix. because the thinning rates of the two polarities are different.

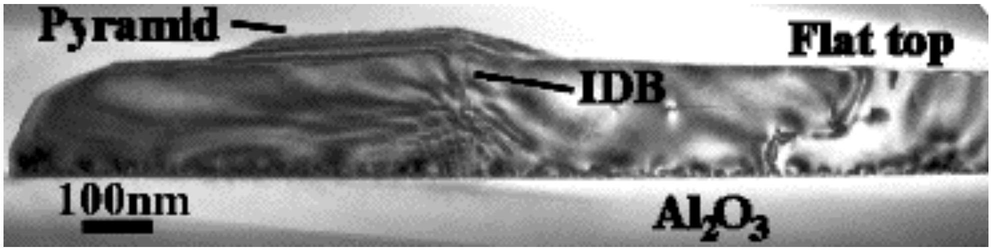

Figure 4. TEM cross-section of a GaN layer containing hexagonal flat tops and a few pyramids. An ID with Ga-polarity is situated at the apex of the pyramid. The flat tops which have a N-polarity do not contain IDs.

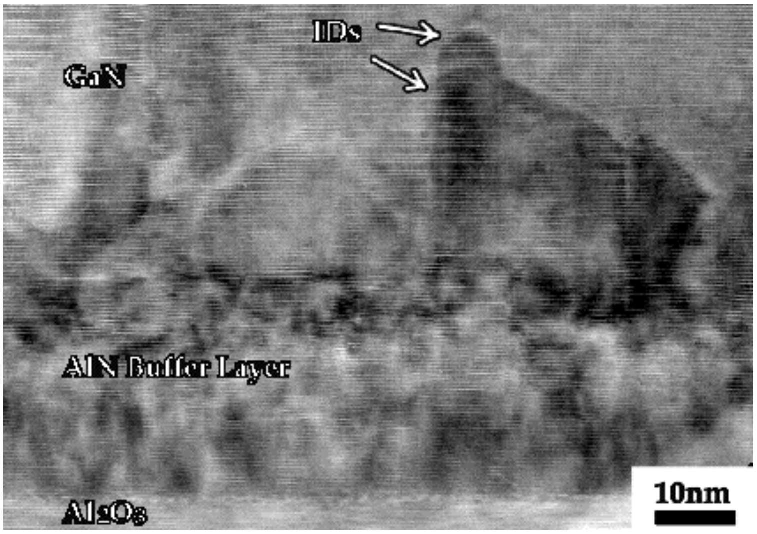

Figure 5. TEM cross-section of a flat GaN layer showing the region near the AlN buffer layer. Domains can be seen. From HREM contrast they look like Inversion Domains that do not propagate in the GaN layer.

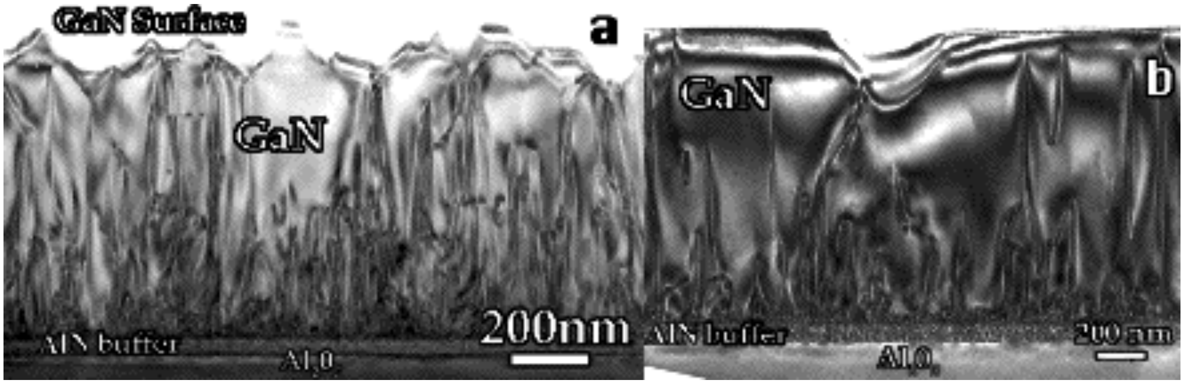

Figure 6. Two beam TEM low magnification images of two samples grown in the same experimental conditions (A-sapphire substrate, AlN 800°C buffer layer annealed at 1000°C) except for the growth temperature of the GaN layer. The layers both have a Ga-polarity. (a) The layer grown at 900°C is very rough and has a tendency to exhibit $\{0\ 1\ \bar{1}\ 0\}$ facets. Dislocations are located at the intersection of the grains. (This sample is similar to the sample of figure 1 (c,f) which was grown on a C-sapphire substrate) (b) The layer grown at 950°C is nearly flat except for a few grooves. It contains only dislocations. The defect density in the AlN buffer layer is very high.