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## TEM CHARACTERIZATION OF GaN NANOWIRES

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### ABSTRACT:

Transmission electron microscopy was applied to study GaN nanowires grown on carbon nanotube surfaces by chemical reaction between Ga<sub>2</sub>O and NH<sub>3</sub> gas in a conventional furnace. These wires grew in two crystallographic directions,  $\langle 2\bar{1}10 \rangle$  and  $\langle 01\bar{1}0 \rangle$  (fast growth directions of GaN), in the form of whiskers covered by small elongated GaN platelets. The morphology of these platelets is similar to that observed during the growth of single crystals from a Ga melt at high temperatures under high nitrogen pressure. It is thought that growth of nanowires in two different crystallographic directions and the arrangement of the platelets to the central whisker may be influenced by the presence of Ga<sub>2</sub>O<sub>3</sub> (based on the observation of the energy dispersive x-ray spectra), the interplanar spacings in the wire, and the presence of defects on the interface between the central part of the nanowire and the platelets surrounding it.

## I. INTRODUCTION

Nanometer scale structures represent an exciting and rapidly expanding area of research. The discovery of carbon nanotubes has drawn interest to the fabrication of one-dimensional materials, such as nanowires and nanorods<sup>1</sup>. One-dimensional materials can play an important role in testing and understanding effects of dimensionality and on the optical, electrical and mechanical properties. Such materials may also have significant applications as interconnects in nanoelectronic devices. GaN and related compounds with wide direct band gaps encompass a broad range of energies in the range of 2-6 eV and are ideal material systems for fabrication of blue/green light emitting diodes<sup>2</sup>, laser diodes<sup>3</sup>, and high power integrated circuits. In the last few years, GaN development has been directed toward thin film applications<sup>2-5</sup>, and only recently have efforts been devoted to other forms of GaN, such as powders, quantum dots, nanorods and nanowires<sup>6-9</sup>.

## II. EXPERIMENTAL

The samples studied here were grown in a conventional furnace with a horizontal quartz tube, similarly to those described earlier<sup>6</sup>. Ga and Ga<sub>2</sub>O<sub>3</sub> were mixed in a weight ratio 1:1. This mixture was placed in a BN crucible and covered by a BN plate with mm channels. Bundles of carbon nanotubes were then placed on the porous BN plate. The crucible was placed in the hot zone inside a quartz tube and held in a mixture of NH<sub>3</sub>( 0.3l/min) and N<sub>2</sub> (1l/min) at 970°C for 1 hr.

Transmission Electron Microscopy (TEM) was used to characterize the resulting nanowires of GaN. Both conventional and high resolution microscopy were applied in this study, supported by Energy Dispersive X-ray Spectrometry (EDX) to determine composition of the samples.

In order to observe the newly grown nanowires, bundles of the C nanotubes were observed under the optical microscope to find the newly grown material which was then placed between two Cu grids for the study by TEM. To determine the lattice spacing of the wires, high resolution images were first taken from the carbon nanotubes as a reference. Fourier transfers were then taken from the outer shells and the central parts of the tube. Based on this internal reference the interplanar distances in the newly grown material could be precisely measured.

### III. RESULTS AND DISCUSSION

Our studies showed that the new material nucleated on the surface of the C nanotubes; no conversion of the C nanotubes into GaN nanotubes or wires was observed. We expected the following reactions to take place which is different from what was suggested by Han et al.<sup>6</sup>



In many areas small agglomerations of amorphous material were observed on the surfaces of the carbon nanotubes (Fig. 1). This amorphous material with large surface area and relatively high surface energy appears to serve as the seed for nucleation of GaN. It can also be speculated that some Ga<sub>2</sub>O nanoplates could have been formed on the surfaces of the carbon nanotubes which were not detected within the amorphous material. Some long GaN nanowires were found to nucleate on the C nanotubes, but their density was rather low (Figs. 2a&b). However, there were some places where their concentration was higher (Fig. 2c). The thicknesses of the nanowires varied and no particular orientation relationship between the C nanotubes and the GaN nanowires existed. The length of the wires was in the range of 7-20

$\mu\text{m}$ . All the observed GaN nanowires were covered by small GaN platelets attached to each other (Figs. 2a&b). The individual platelets had an elongated hexagonal shape, similar to the bulk crystals grown at high temperature ( $1500^\circ\text{C}$ ) under high pressure (15-18kbars) of nitrogen.<sup>10,11</sup> The long axis of each platelet was about 130 nm and the width about 90 nm.

For the thinner nanowires (60-90 nm in diameter) it was possible to obtain high resolution TEM images from the platelets with zone axes closest to the neutral position of the goniometer. Two sets of planes with interplanar spacings of 2.44 Å and 2.35Å and an  $80^\circ$  angle between them were observed with one of these planes parallel to the long edge of the platelet (Fig. 2b-inset). This angle is in good agreement with the calculated angle of  $80.35^\circ$  between the (1011) and (1101) planes of GaN. The ratio of their interplanar spacings would need to be 1 which is close to the experimental ratio, 1.04. An interplanar ratio of 1.07 and the angle  $81.45^\circ$  is also possible for the (1123) and (2022) planes of  $\alpha\text{-Ga}_2\text{O}_3$  ( $a=4.979\text{\AA}$  and  $c=13.429\text{\AA}$ ), but the agreement with experimental values is much better for GaN. However, slight modification of the lattice spacings of GaN by  $\text{Ga}_2\text{O}_3$  can not be excluded. The edges of platelets were inclined by about  $18^\circ$  to the growth direction of the wire, which agrees well with  $\langle 2110 \rangle$  as the growth direction of the wire.

However, for the wider wires (about 400 nm in diameter) a much larger angle (about  $60^\circ$ ) between the wire growth direction and the long axis of the platelets was observed (Fig. 2c). When such thick wires were tilted, one could observe that the platelets were arranged on two sides of the central part, which seen edge-on had a slightly different contrast, indicating thinner area of the central part of the wire (Fig. 3a). EDX studies showed that no substantial difference could be seen in the composition of the outside platelets and the central parts and that their composition was that of GaN (Fig. 4a-d). In the central part of the thicker wires (about 50-60 nm wide) a slightly higher intensity of N was observed (Fig. 4c –spectrum taken from the area 3 on Fig. 3a). This is typical for analysis in a thinner area, since N, as a lighter

element, is more absorbed in thicker parts, e.g. platelets surrounding such a wire. Some traces of oxygen can not be excluded, particularly at the transition areas between the central part and the outside platelets (Figs. 4b and c).

For the plates located on the outside of the central part of the thicker wire (such as on Figs. 3a and b) wurtzite GaN lattice images with the  $[2\bar{1}10]$  zone axis can be observed (Fig. 3b), confirming that these plates are monocrystalline. Based on the Fourier transform of this lattice image of Fig. 3b and comparison to the spacings obtained for a carbon nanotube, the observed ratio of the two perpendicular lattice spacings (0002) and  $(01\bar{1}0)$  was 1.04 compared to the expected values for bulk GaN of 1.07, which is a good agreement. The measured lattice distances for GaN varied slightly from those found in tables, e.g. 2.5 Å instead of 2.585 Å for (0002) and 2.65 Å instead of 2.754 Å for  $(01\bar{1}0)$ . Only one set of lattice planes with interplanar distance of 2.65 Å was observed in this orientation for the central part of the wire (Fig. 3c). This is close to the 2.754 Å expected for  $(01\bar{1}0)$  of GaN. A small angle between the  $(01\bar{1}0)$  planes of the outside GaN platelets and the central part can be detected. Since the outside platelets are observed in the  $[2\bar{1}10]$  zone axis parallel to the electron beam, the growth axis of the thicker wire observed on Fig. 3a must be perpendicular, and therefore be the  $[01\bar{1}0]$  direction. This shows that the thicker wires grow with a different growth direction than the thinner wires and that the outside platelets were growing with (0002) planes attached to the central part of the nanowire. The areas between the central part of the wire and the outside platelets contained many planar defects (see the area in the upper part of Fig. 3c and high resolution images from other places of such regions on Figs. 5 a-c). In some places areas of the cubic structure can be observed (Fig. 5c), and in others some ordering is observed on  $\langle 01\bar{1}1 \rangle$  planes (Fig. 5b). The ordering is probably influenced by the presence of oxygen. Presence of these defects would explain why a small angle between the  $(01\bar{1}0)$  planes of the outside platelets and the similar planes in the central wire would be formed. The reason why wires

grew in two different crystallographic directions might also be related to the composition of the wires since modification of the interplanar spacing ( $2.65\text{\AA}$  instead of  $2.75\text{\AA}$ ) by oxygen incorporation cannot be excluded.

The thinner nanowires (such as Fig. 2a&b) where the edges of the platelets formed an angle of about  $18^\circ$  with the  $\langle 2\bar{1}10 \rangle$  growth direction confirms that this is the fast growth direction of GaN, as observed for platelets grown under high hydrostatic pressure<sup>10,11</sup>. The fact that these platelets are not precisely aligned in this direction might be related to oxygen contamination and the defects formed in the interfacial areas between the central wire and the surrounding platelets.

The detailed wire growth mechanism is still not determined. It appears that newly arrived atoms tend to migrate to the tip of the wire and fast growth takes place only in this area. Only in a later stage of growth is the formation of the platelets expected. The coexistence of wires and platelets was already reported in the early work of He et al<sup>12</sup>. These authors believe that, during decomposition of  $\text{NH}_3$ , Ga and N can form GaN molecules and build a dark-gray amorphous GaN matrix which is perhaps similar to that observed in our studies (see Fig. 1). According to these authors, in a second stage of growth very thin hexagonal plates can grow in the form of polycrystalline hillocks on the surface of the growth container and finally a wire can start to grow from the side of the plate but not from its surface. Our studies suggest that first a whisker would grow and then small platelets will be formed on the surface of the whisker at a later stage of growth. Bootsma and Gassen<sup>13</sup> reported enhancement of the growth of silicon and germanium whiskers as an effect of impurities and suggested a vapor-liquid-solid mechanism (VLS). Two mechanisms VLS and vapor-solid (VS), were revealed for SiC whiskers<sup>14</sup> and a tendency for time-saturation was observed. Kaneko<sup>15</sup> reported axial growth of iron whiskers to be time-saturated and independent of the growth temperature. Since studies of

the growth of GaN nanowires are in a preliminary stage much more work is required to fully understand the growth mechanism of these nanowires.

#### IV. CONCLUSIONS

The structure of GaN nanowires is reported. Wires having two different thicknesses (about 90 nm and 400 nm in diameter) and different growth directions  $\langle 2\bar{1}10 \rangle$  and  $\langle 01\bar{1}0 \rangle$ , respectively, were observed. It appears that they consisted of central parts, most probably growing as whiskers, and small hexagonal platelets subsequently grown on their surfaces. Defects, modulated structures and occasionally cubic material were observed especially in the interfacial areas between the central parts of the wires and the surrounding platelets. Interplanar distances in the platelets grown on the surface of the wires agree well with the values of GaN (2.5Å compared to 2.585Å for (0002) GaN table value and 2.65Å instead of 2.75Å for (01 $\bar{1}$ 0) GaN table value). It appears that oxygen presence from Ga<sub>2</sub>O<sub>3</sub> might slightly modify interplanar distances in these wires. Both the possibility of oxygen presence and defect formation could lead to different orientation relationships between the central parts of the wires and the platelets formed on their surface. We believe that these first results are promising for obtaining this important material in the form of well defined one dimensional nanostructures.

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## FIGURE CAPTIONS:

Fig. 1. Formation of an amorphous “cloud” of GaN on the surface of a C nanotube.

Fig. 2. (a & b ) GaN nanowires showing the alignment of the platelets. An inset in (b) shows the lattice image from the indicated area. The arrow shows the growth direction (GD) of the wire. The angle of  $80^\circ$  observed in the platelet is marked between  $(10\bar{1}1)$  and  $(11\bar{0}1)$  planes of GaN. (c) Thicker wires with a larger angle between the long axis of the platelets and the growth direction of the wire.

Fig. 3 (a) GaN nanowire in edge-on orientation with marked growth direction (GD) of the wire. Note lighter contrast in the central part of the wire (marked by c). The platelets are arranged on both sides of the wire. The numbers 1- 4 indicate the places where EDX analysis was performed; (b) High resolution images from the platelet marked by b with the  $[2\bar{1}10]$  zone axis. The  $90^\circ$  angle is observed between  $(0002)$  planes parallel to the growth direction GD and  $(01\bar{1}0)$  planes; (c) High resolution image of the central part of the wire marked in (a) by the box with c. Only one set of planes is visible. Note distortion of these planes in the interfacial area between the wire and the surrounding platelets observed in the upper part of the micrograph. Growth direction (GD) of the wire is indicated.

Fig. 4. EDX analysis across the wire, the approximate areas (1-4) where analysis was performed is shown on Fig. 3a; (a) shows the whole spectrum from the area 1. Note lack of any heavy elements; (b-d) only low energy spectra are shown indicating the presence of N and some traces of oxygen together with the Ga  $L\alpha$  peak.

Fig. 5. (a) High resolution image of defects formed in the area between the central part of the wire and platelets; the angle  $65^\circ$  is measured between  $(10\bar{1}1)$  planes with the interplanar distances of  $2.25\text{\AA}$  ( $2.44\text{\AA}$ -table value) and  $(01\bar{1}0)$  planes with the interplanar distances  $2.65\text{\AA}$  ( $2.76\text{\AA}$  table value). The calculated angle between these planes should be  $63.8^\circ$  and the ratio of the interplanar distances 1.13 which is in a good agreement with the ratio of 1.18 obtained from the measured values. Small deviations might be introduced by oxygen; (b) Ordered structures formed on the  $(10\bar{1}1)$  planes in the area between the central wire and a platelet; (c) Lattice image from another area with cubic GaN. The angle between  $(111)$  planes is marked.

Fig. 1

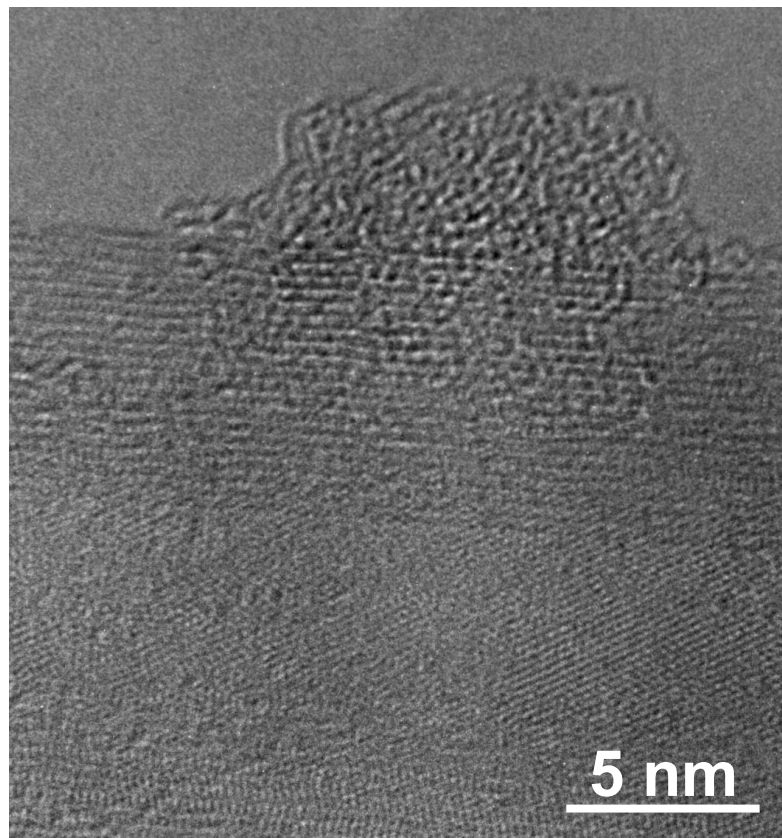


Fig. 2

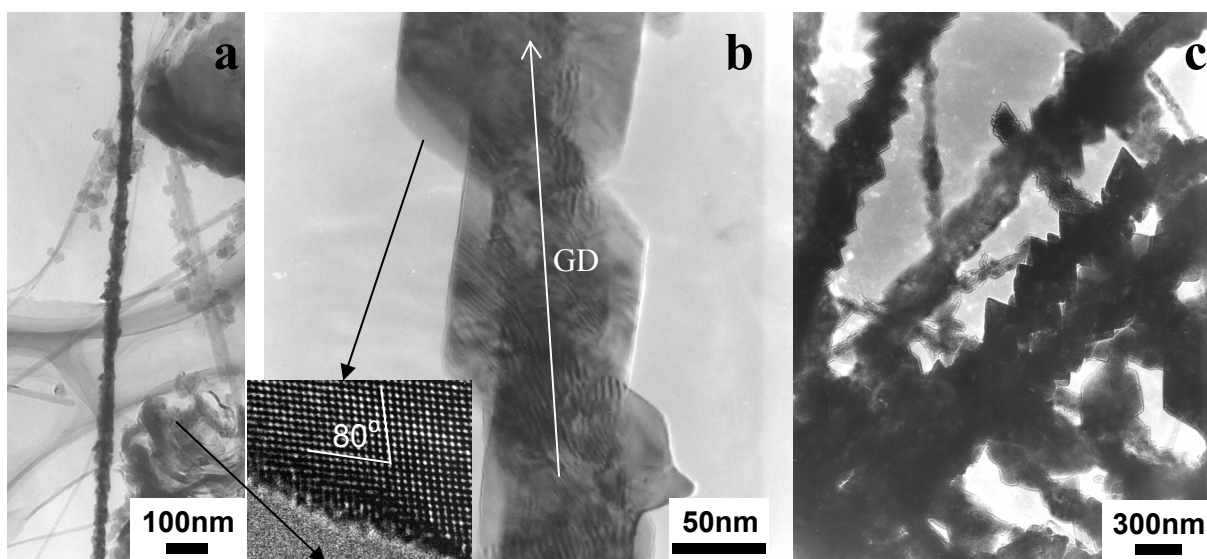


Fig. 3

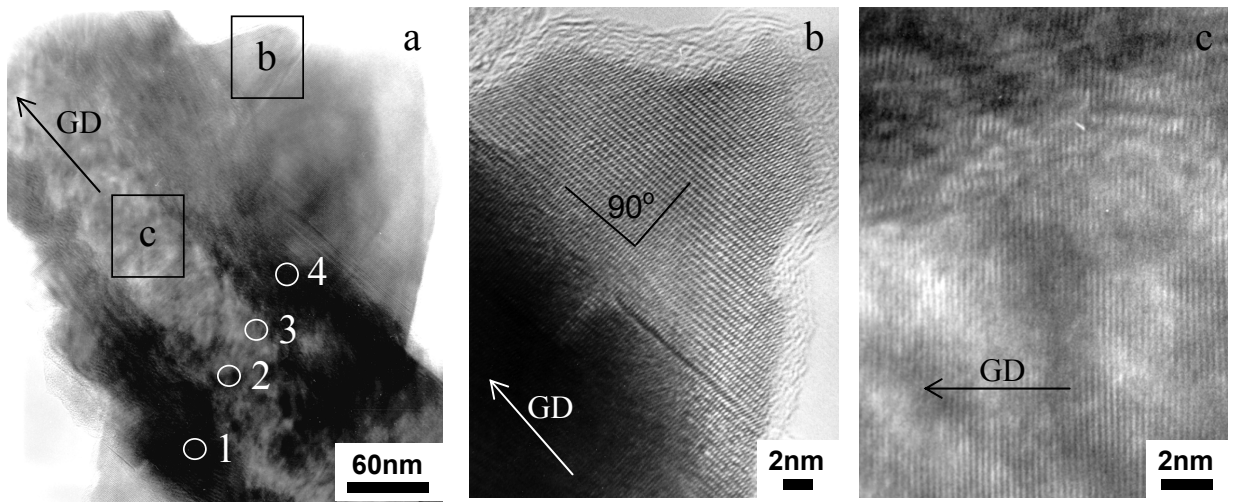


Fig. 4



Fig. 5

