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One-dimensional GaN nanomaterials transformed from one-dimensional Ga_2O_3 and Ga nanomaterials

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One-dimensional (1D) GaN nanomaterials exhibiting various morphologies and atomic structures were prepared via ammoniation of either Ga_2O_3 nanoribbons, Ga_2O_3 nanorods or Ga nanowires filled into carbon nanotubes (CNTs). The 1D GaN nanomaterials transformed from Ga_2O_3 nanoribbons consisted of numerous GaN nanoplatelets having the close-packed plane, i.e. $(0002)_{2H}$ or $(111)_{3C}$ parallel to the axes of starting nanoribbons. The 1D GaN nanomaterials converted from Ga_2O_3 nanorods were polycrystalline rods covered with GaN nanoparticles along the axes. The 1D GaN nanomaterials prepared from Ga nanowires filled into CNTs displayed two dominant morphologies: (i) single crystalline GaN nanocolumns coated by CNTs, and (ii) pure single crystalline GaN nanowires. The cross-sectional shape of GaN nanowires were analyzed through the transmission electron microscopy (TEM) images. Formation mechanism of all-mentioned 1D GaN nanomaterials is then thoroughly discussed.

Keywords: GaN; One-dimensional; Ga_2O_3; Nanostructures

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GaN is a wide diret-bandgap (3.39 eV at room temperature) semiconductor material and its one-dimensional (1D) structure has a high potential for applications in blue and UV light-emitting and laser diodes as well as in high temperature and high power electronic devices [1,2]. Up to date, the synthetic approaches for 1D GaN nanomaterials have relied on various physical or chemical methods, such as carbon nanotubes (CNTs) [3-5] and anodic alumina membrane [6,7] template-originated methods, Fe, Co, Ni and Au metal- catalyst vapor-liquid-solid (VLS) growth [8-10], SiO_2, Fe_2O_3, and B_2O_3 oxide-assisted growth (OAG) [11,12], Precursor- based methods metalorganic chemical vapor deposition (MOCVD) [13], and hydride vapor phase epitaxy (HVPE) [14].

Although the above-mentioned groups are different from each another, all methods are capable of generating 1D GaN nanomaterials with a characteristic single-crystalline structure. Liliental-Weber [15] and Lan [16] have reported preferentially-oriented 1D GaN nanomaterials consisting of small GaN platelets. Furthermore, Zhao [17] and Ogi [18] have studied the influence of starting materials Ga_2O_3 powders (particles) on growth of GaN nanomateials. Though the formation mechanism of the GaN nanomaterials has been discussed, the reason behind the orientated growth remains unclear. Our current investigation sheds an additional light on this issue. In addition, the design, synthesis, and characterization of surface-modified nanostructures are of fundamental importance in controlling the mesoscopic properties of new materials and in developing new tools for nanofabrication. So we expect that presently synthesized GaN 1D nanomaterials coated with GaN nanoparticles are capable of bringing new electronic characteristics different from those displaying by their simple mechanical mixtures due to somewhat specific boundary

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electron conditions.

GaN nanoribbons consisting of platelets were fabricated in a conventional furnace with a horizontal quartz tube. Ga and Ga_2O_3 powders were homogeneously mixed in a weight ratio 1:1. The mixture was placed in a BN crucible and covered by a BN plate with drilled mm-size channels. Bundles of CNTs were placed on the BN plate. The synthesis process was performed in two steps. First, the furnace was washed with a N_2 gas (3 l/min) over ~2 hours under gradual heating to 900°C. Second, a mixture of NH_3 (0.3 l/min) and N_2 (1 l/min) was substituted for the original N_2 gas flow while the temperature was gradually increased to 970°C over 10 min and then kept constant during 30 min. Then, the whole quartz tube was taken out from the furnace and cooled to the room temperature. We found that the surface of the starting CNTs was covered with a thin layer of yellow-colored material.

Firstly, Ga_2O_3 nanorods and Ga-filled CNTs were synthesized in a vertical radio-frequency furnace by mixture of Ga_2O_3 and pure amorphous active carbon. (see also Refs. [19, 20]) The furnace was heated at 1360°C over 1-2 h. Ga-tipped Ga_2O_3 nanorods were found to be deposited on the outer surface of the C fiber coat where the temperature was estimated to be approximately 1000°C. Meanwhile, Ga-filled CNTs were collected from the inner surface of the outlet pipe of the furnace where the temperature was estimated to be ~800°C. Then, place Ga_2O_3 nanorods and Ga-filled CNTs into the conventional furnace for ammoniation at 970°C (described above), respectively. Finally all the resultant materials were collected and studied by a 300 kV field emission analytical high-resolution transmission electron microscope (HRTEM, JEM-3000 F) equipped with an X-ray energy dispersive spectrometer (EDS).

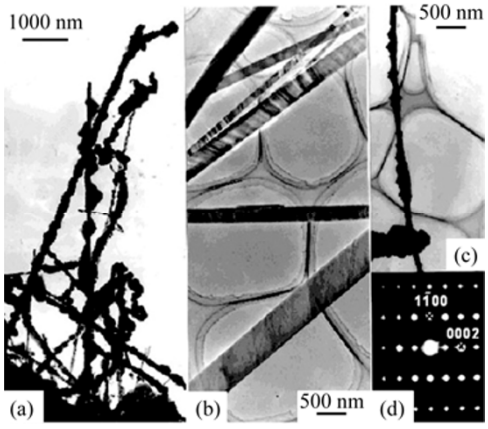

FIG. 1. (a) Morphology of the yellow-colored materials synthesized in a NH_3 atmosphere. (b) Morphology of the white-colored materials synthesized in a N_2 atmosphere. (c) A GaN nanoribbon transformed from a Ga_2O_3 ribbon and its [1120] diffraction pattern in (d).

Figure 1(a) depicts the morphology of the yellow-colored materials synthesized via a reaction Ga and Ga_2O_3 powders with NH_3. They have widths of 40-100 nm and lengths of up to 10 μm. The materials were detected to be 1D nanoribbons consisting of numerous nanoplatelets. An energy dispersion spectroscopy (EDS) analysis indicated that the nanoribbons are composed of Ga and N. It is believed that two processes are involved in the growth of the nanoribbons: (i) Ga_2O_3 nanoribbons are crystallized on the surface of CNTs, and, while a N_2 gas having impurities of O_2, is introduced into the furnace, the chemical reactions proceed as follows:

$$Ga_2O+O_2 \rightarrow Ga_2O_3 \quad (1.a)$$

where a Ga_2O vapor is generated in line with the reaction described by Han et al [3].

$$Ga_2O_3+4Ga \rightarrow 3Ga_2O \quad (1.b)$$

The vapor cannot be oxidized further after it reaches the surface of CNTs, because the CNTs serve as a shelter for the O_2 impurity in N_2 gas; (ii) Ga_2O_3 nanoribbons are transformed into GaN nanoribbons while NH_3 is introduced into the furnace; the involved reaction may be written as follows,

$$Ga_2O_3+2NH_3 \rightarrow GaN+3H_2O \quad (2)$$

where GaN platelets may initially nucleate on the side-surface of a Ga_2O_3 nanoribbon and the subsequent growth of GaN platelets propagates along the whole nanoribbon.

To confirm the growth mechanism of the yellow-colored Ga_2O_3 nanoribbons, we carried out additional experiments. Before the second step, we examined a thin layer of the white-colored materials on the surface of CNTs. The materials were determined to be Ga_2O_3 nanoribbons having morphologies depicted in Fig. 1(b). After ammoniation of the Ga_2O_3 nanoribbons at 970°C, we found that the color of the materials was changed from white to yellow. The later materials were

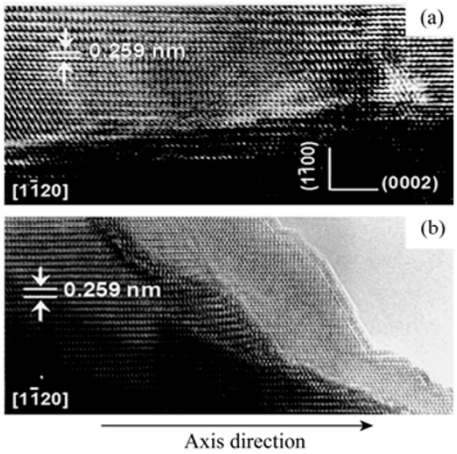

FIG. 2. (a) [1120] HRTEM image of a platelet on a nanoribbon in Fig. 1(a), and (b) [1120] HRTEM image of a platelet on the nanoribbon in Fig. 1(c). There is a common characteristic in the two images: a thicker GaN platelet is under a thinner GaN platelet with the $(0002)_{2H}$ stacking plane.

found to be GaN. There were nanoribbons covered with nano-platelets. A nanoribbon is shown in Fig. 1(c), its axis is parallel to the (0002) plane, as shown in Fig. 1(d), which is the $[11\bar{2}0]$ zone axis diffraction pattern. The similarity between the morphologies in Fig. 1(a) and Fig. 1(c) suggests that the proposed growth mode for the nanoribbons depicted in Fig. 1(a) is correct. The reasonability of the proposed growth mode may require other evidence additive to the fact of similar morphologies of the two kinds of the GaN nanoribbons. Detailed HRTEM investigation may become effective.

Figure 2(a) and (b) are the $[11\bar{2}0]$ HRTEM images of two platelets on a nanoribbon in Fig. 1(a) and that in Fig. 1(c), respectively. The two images have one characteristic in common - a thicker GaN platelet laying under a thinner GaN platelet with the $(0002)_{2H}$ stacking plane. Figure 3(a) and (b), $[1\bar{1}0]$ HRTEM images of two platelets on a nanoribbon in Fig. 1(a) and that in Fig. 1(c), also showing that a thicker GaN platelet is under a thinner GaN platelet with the $(111)_{3C}$ stacking plane. In the four HRTEM images, the close-stacking (0002) and/or (111) planes are parallel to the axis direction of the nanoribbons. The relationship can be explained in terms of the growth mode schematic of GaN nucleation shown in Fig. 4. When GaN islands nucleate on a certain side surface of a Ga_2O_3 nanoribbon, their close packing planes stack to the side surface of a certain plane, resulting in the axis parallel to the stacking plane.

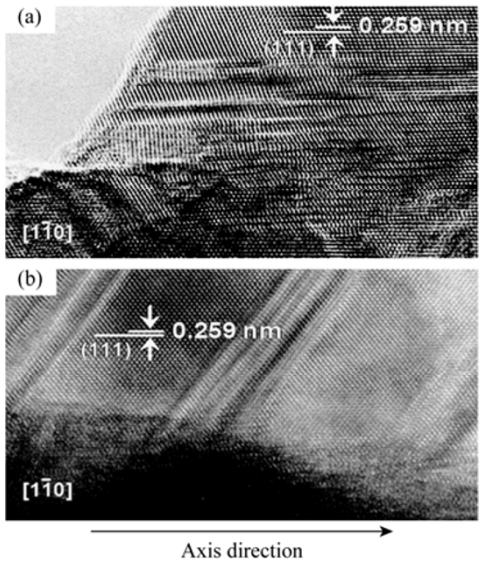

FIG. 3. (a) [110] HRTEM image of a platelet on the nanoribbon in Fig. 1(a), and (b) [110] HRTEM image of a platelet on the nanoribbon Fig. 1(c). There is also a common characteristic in two images: a thicker GaN platelet is under a thinner GaN platelet with the $(111)_{3C}$ stacking plane.

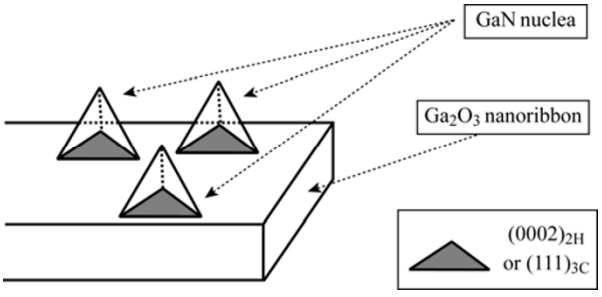

FIG. 4. A schematic of Ga_2O_3 to GaN conversion during an initial transformation stage. GaN nucleates on a side surface of a nanoribbon with its close-packed plane stacked to the side surface of a certain plane, resulting in the axis parallel to the stacking plane.

Figure 5(a) shows the morphology of Ga-tipped Ga_2O_3 nanorods, which were found to have a round cross-section under tilting experiments in TEM. After ammoniation, the Ga_2O_3 nanorods and their spherical tips were transformed to GaN nanorods with spherical GaN tips. Generally the rods were covered by numerous nanoparticles, as shown in Fig. 5(b) and 5(c), respectively. The GaN nanorods were polycrystalline and have no preferred axis direction. These nanorods are different from the GaN nanoribbons converted from Ga_2O_3 nanoribbons, which have a definite axis direction parallel to the $(0002)_{2H}$ and/or $(111)_{3C}$ planes. The origin of this phenomenon can be

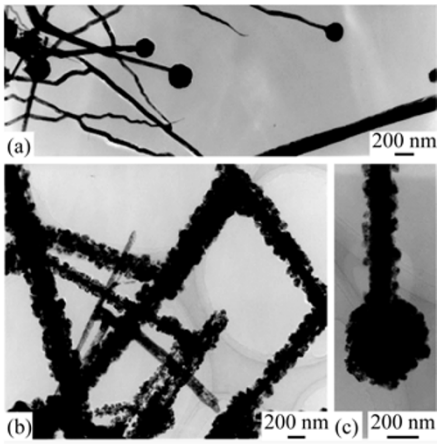

FIG. 5. (a) Morphology of Ga-tipped Ga_2O_3 nanorods. (b) Morphology of GaN nanorods consisting of numerous GaN nanoparticles on their surface. (c) Morphology of a spherical GaN tip consisting of numerous GaN nanoparticles.

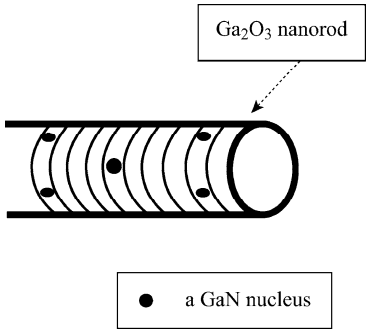

FIG. 6. A schematic of an initial stage of transformation from a Ga_2O_3 to a GaN nanorod. GaN randomly nucleates on the round side surface at numerous sites, resulting in a GaN nanorod with numerous particles.

explained through a schematic diagram, Fig. 6. During the transformation, randomly-oriented GaN domains nucleate on a round side surface at numerous sites finally resulting in a polycrystalline GaN nanorod.

Figure 7(a) depicts the morphology of a Ga nanowire filled into CNT. After ammoniation, a Ga nanowire can be transformed to GaN nanocolumns coated by CNTs, as shown in Fig. 7(b). Figure 7(c) and d are the EDS spectra taken from the pre- and post-transformed Ga nanowires, respectively. HRTEM study illustrates that each GaN nanocolumn is single crystalline. Figure 7(e) shows a HRTEM image of such single-crystalline GaN nanocolumn coated by C layers.

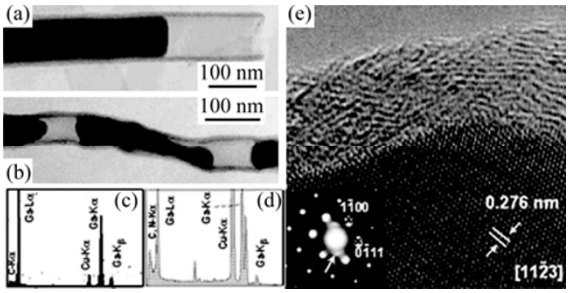

FIG. 7. (a) Morphology of a Ga nanowire filled in CNT. (b) Morphology of GaN nanocolumns coated by CNTs and transformed from a Ga nanowire filled into CNT. (c) and (d) EDS spectra of a Ga nanowire and a GaN column filled in CNT, respectively. (e) HRTEM image of a GaN column filled in a CNT.

The formation of GaN nanowires filled in CNTs can be explained as direct ammoniation of Ga nanowires filled in CNTs. However, such explanation may find a better proof if a pure GaN nanorod not covered with a CNT may be found in the ammonia-treated materials. In fact, such material was found, as shown in Fig. 8(a). This rod has an axis perpendicular to the $(1\bar{1}00)$ plane, as displayed in Fig. 8(b) and (c). The most intriguing fact is that new contrast fringes appear in Fig. 8(a). It is believed that the fringes are originated from the thickness difference [21]. According to this, we can conjecture that the cross-section of the rod may have two kinds of possible shapes shown in Fig. 9. The above-presented analysis made us possible to estimate the thickness and the cross-section shape using the observed contrast fringes. It is noted though that a more definite confirmation using a slice method of cross-section is probably needed [22].

The formation of a pure GaN nanorod can also be explained due to ammoniation of Ga in CNTs. When a metallic Ga with a density of ~5.90 g/cm^3 is gradually transformed to GaN with a density of ~5.90 g/cm^3, the volume increased by 20% as the molecular weight increased by 20%. This extra volume part gradually grows and leads to a resultant pure GaN

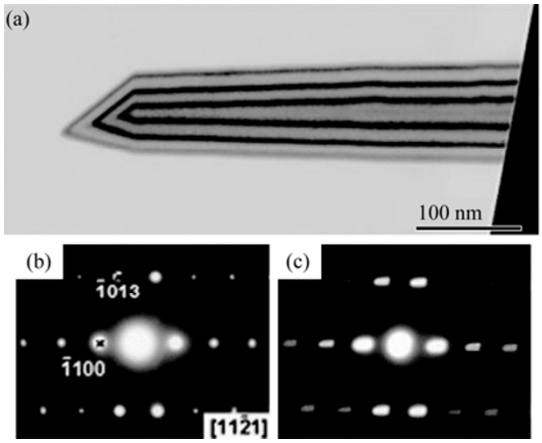

FIG. 8. (a) TEM image of a pure GaN nanorowire. (b) and (c), diffraction patterns focus and defocus [11 $\bar{2}$ 1] zone axis, respectively, which show that the GaN can be indexed as 2H structure with its axis along [1 $\bar{1}$ 00] direction.

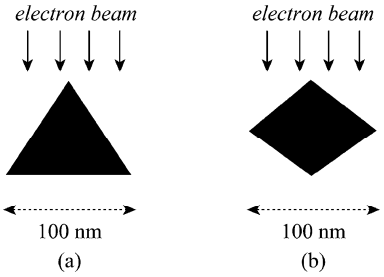

FIG. 9. Two kinds of possible cross-sectional shapes of the pure GaN nanowire in Fig. 8(a).

nanorod whose cross-section may become non-round as compared to a round shape of the initial Ga nanorod.

To sum up, the presented transformation scheme consists of two steps and relies on conversion of a given 1D material to another 1D material in a given gaseous atmosphere. This approach has been used to synthesize ZnS [23] and GaN nanotubes [24, 25]. It is believed here that the process is an important practical method to synthesize novel 1D material and to fabricate complicated arrays of those with nanoparticles.

We fabricated one-dimensional GaN nanoribbons, nanorods, and nanowires through ammoniation of Ga_2O_3 nanoribbons, Ga_2O_3 nanorods and Ga nanowires filled in CNTs, respectively. The GaN nanoribbons consist of numerous GaN nanoplatelets with the close-packed planes, i.e. $(0002)_{2H}$ or $(111)_{3C}$ being in parallel with the axis of nanoribbons. The GaN nanorods obtained from Ga_2O_3 nanorods are polycrystalline nanorods attaching numerous GaN nanoparticles along their axes. GaN nanowires coated with CNT layers were single-crystalline. The thickness and cross-sectional shape of a pure GaN nanowire may be calculated and conjectured according to the thickness fringes in its transmission electron

microscopy image. Formation mechanisms of 1D GaN nanomaterials are believed to be governed through inhering corresponding 1D characteristics of the starting Ga_2O_3 and Ga materials, whereas the nucleation during initial transformation stage may result in new nanoparticle formation.

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