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LETTER TO THE EDITOR

Gallium nitride nano-ribbon rings

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Abstract

Gallium nitride (GaN) nano-ribbon rings were formed through a simple sublimation method. They were characterized by x-ray powder diffraction (XRD), field emission scanning electron microscopy (FE-SEM), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). FE-SEM images showed that the GaN rings had diameters of about $2 \sim 10$ μm. XRD, SAED and HRTEM indicated that the rings were wurtzite GaN single crystals.

The pioneering work by Iijima in making carbon nanotubes has aroused much research interest worldwide to synthesize nanoscale materials of various elements and compounds because of their potential uses in both mesoscopic research and development of nanodevices [1, 2]. Wurtzite structure gallium nitride is a wide band gap semiconductor with a tremendous range of possible applications. It has a direct band gap of 3.4 eV at room temperature, which makes it suitable for blue light emitting devices, including light emitting diodes and laser diodes [3, 4]. A great deal of attention has been focused on the study of low-dimensional GaN materials with nanometer sizes because of their potential to test and understand fundamental concepts about the roles of dimensionality and size in optical and electrical properties and for application in the semiconductor industry [5–10].

When individual molecules or particles aggregate into ordered structures, the symmetries of the resulting superstructures are often determined by the sub-unit shape, such as spheres, rods and disks. A ring is a superstructure that would not be predicted to form from any of these three simple shapes. However, under certain specific conditions the dominant structure formed by all these sub-unit shapes is a ring [11]. The ring-forming experiments have been carried out on a diverse set of materials. Smalley's group and Martel *et al* reported that they had observed ring-shaped carbon nanotubes [12, 13].

In an attempt to grow a one-dimensional GaN structure using a sublimation process on polished quartz glass substrates, GaN nano-ribbon rings were formed. To our knowledge, GaN rings have not been reported to date. In this letter, we report the fabrication of them.

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The method involves a two-step process. First, we treated the hexagonal gallium nitride powder with a purity of at least 99% by a mechanical deformation process [14], which was carried out in a home-made rolling laboratory ball mill using hardened agate balls with a diameter of 8 mm and an agate cell for 30 hours. The GaN powder was produced in our laboratory by a conventional gas reaction method, the details can be found elsewhere [15]. The containment cell was loaded with 10 g of GaN powder together with 16 agate balls. After milling, as-milled powders and a polished quartz glass substrate with a separation of 10 mm were loaded into the centre of a horizontal quartz glass tube inside a tube furnace. The quartz tube was first pumped, then filled with inert argon gas, then re-pumped. This operation was repeated four times. After that, the quartz tube was heated under the flow of argon of about 50 cubic centimeters per minute to allow degassing. When it reached 940 °C, a flow of NH_3 about 15 cubic centimeters per minute was switched on and kept for 150 minutes, the purity of the ammonia was better than 99.9%. After cooling, a thin light yellow layer on the substrate was formed.

The x-ray powder diffraction (XRD) of the light yellow layer was characterized using a Rigaku (Tokyo, Japan) D/max-2400 x-ray diffractometer with CuKα radiation. Figure 1 shows a typical powder XRD pattern of the layer and reveals that hexagonal wurtzite GaN is obtained. The positions of the XRD peaks show good agreement with those of the hexagonal wurtzite GaN with lattice constants $a = 0.3186$ nm and $c = 0.5178$ nm listed in the standard handbook of XRD spectra.

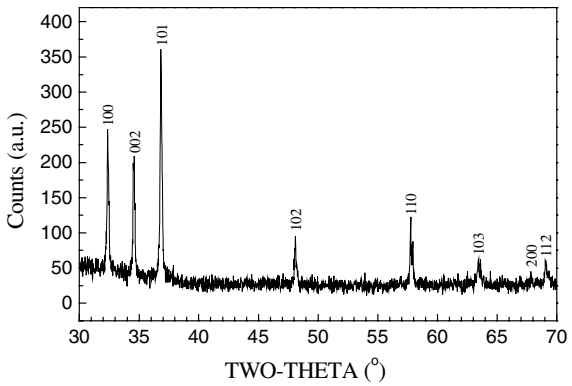

Figure 1. XRD pattern of the GaN nano-ribbon rings (deposited on quartz glass substrate) using CuKα radiation.

The morphologies of the products were observed by a Hitachi (Tokyo, Japan) S-4200 field emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectrum (EDS). Figure 2 shows that the thin layer on the quartz glass substrate is composed of nano-ribbon rings. The diameters of the rings are about $2 \sim 10$ μm. The width and the thickness of the nano-ribbons that make up the rings are $60 \sim 400$ nm and $10 \sim 60$ nm respectively. EDS measurements show that the rings consist of Ga and N with an atomic ratio of 1:1, corresponding to the chemical composition of GaN. In contrast, the FE-SEM image of the as-milled GaN powders before heating is shown in figure 3, which consists of particles with diameters of about $35 \sim 150$ nm.

The typical selected area electron diffraction (SAED) pattern (figure 4) and high-resolution transmission electron microscopy (HRTEM) lattice image (inset in figure 2) of a section of an individual GaN ring were taken on a Jeol-2010 transmission electron microscopy. The SAED

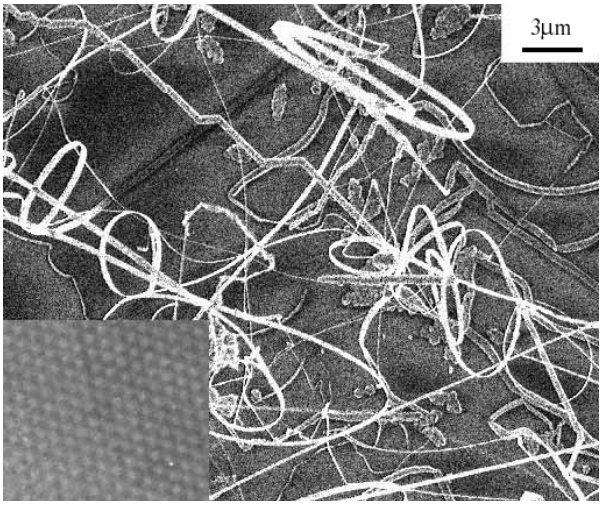

Figure 2. FE-SEM image of the GaN nano-ribbon rings deposited on quartz glass substrate, inset is the HRTEM image of a section of a GaN ring.

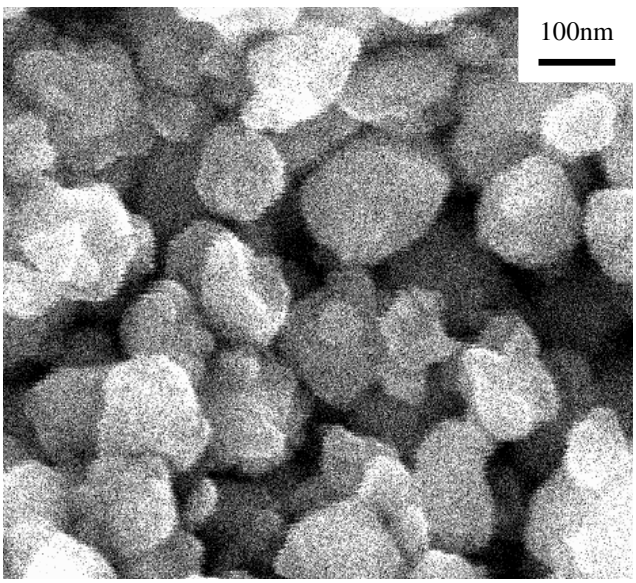

Figure 3. E-SEM image of the as-milled GaN powders before heating.

pattern can be indexed based on a hexagonal cell with lattice parameters of $a = 0.318$ nm and $c = 0.518$ nm, consistent with above x-ray powder diffraction results, it confirms that the ring are single crystal wurtzite GaN. The electron beams are parallel to [011]. No diffraction features of nanotube structure were identified [16], instead, the nano-ribbon ring is solid. The HRTEM image also indicates that the nano-ribbon ring is solid, not hollow.

GaN rings are not observed in milled samples before heating. The above results clearly show formation of GaN nano-ribbon rings during annealing of milled GaN particles at 940 °C. Ogino *et al* reported that needle-like GaN crystals can be grown by sublimation at above

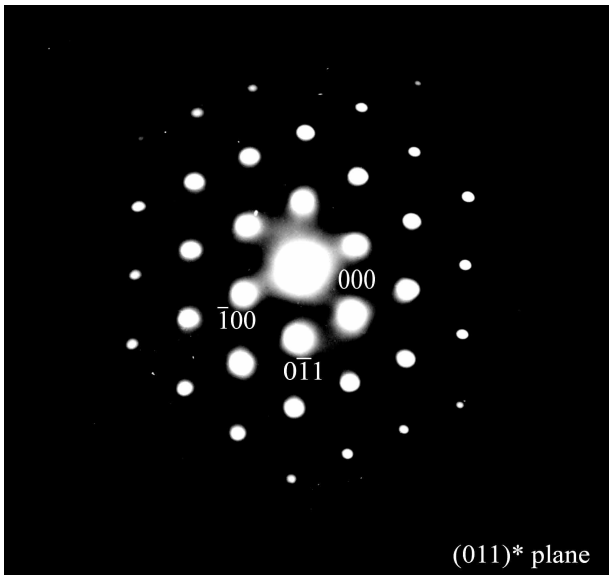

Figure 4. SAED pattern of a GaN nano-ribbon ring.

1500 °C [17, 18]. Using the method described in this letter, we formed GaN nano-ribbon rings from as-milled GaN powders at a relatively low temperature. Goldstein *et al* reported that the melting point of nano-particles is much lower than that of the bulk material [19]. Milled GaN powders have very high specific surfaces and are metastable in thermal annealing process, which make it easy to sublimate and precipitate to fabricate rings. To test this, we annealed non-milled GaN powders with the same condition, and found no rings. The milling process before annealing is the key to the formation of GaN rings on polished quartz glass substrates through this relatively low temperature sublimation method.

In conclusion, gallium nitride nano-ribbon rings were fabricated by a simple sublimation method. They were characterized by XRD, FE-SEM, EDS, SAED and HRTEM methods. FE-SEM images showed that the rings had diameters of about $2 \sim 10\ \mu$m. XRD, EDS, SAED and HRTEM indicated that the rings were wurtzite GaN single crystals. The present approach may be expanded to form nano-ribbon rings of other materials for use in fundamental research and technological applications.

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References

[1] Iijima S 1991 *Nature* **354** 56
[2] Wong K W, Zhou X T, Au F C K, Lai H L, Lee C S and Lee S T 1999 *Appl. Phys. Lett.* **75** 2918
[3] Nakamura S 1998 *Science* **281** 956
[4] Brown S A, Reeves R J and Haase C S 1999 *Appl. Phys. Lett.* **75** 3285
[5] Xie Y, Qian Y, Wang W, Zhang S and Zhang Y 1996 *Science* **272** 1926
[6] Han W Q, Fan S S, Li Q Q and Hu Y D 1997 *Science* **277** 1287
[7] Cheng G S, Zhang L D, Zhu Y, Fei G T, Li L, Mo C M and Mao Y Q 1999 *Appl. Phys. Lett.* **75** 2455
[8] Duan X and Lieber C M 2000 *J. Am. Chem. Soc.* **122** 188

[9] Chen C C and Yeh C C 2000 *Adv. Mater.* **12** 738
[10] Chen X L, Li J Y, Cao Y G, Lan Y C, Li H, He M, Wang C Y, Zhang Z and Qiao Z Y 2000 *Adv. Mater.* **12** 1432
[11] Vossmeyer T, Chung S W, Gelbart W M and Heath J R 1998 *Adv. Mater.* **10** 351
[12] Liu J, Dai H J, Hafner J H, Colbert D T, Smalley R E, Tans S J and Dekker C 1997 *Nature* **385** 780
[13] Martel R, Shea H R and Avouris P 1999 *Nature* **398** 299
[14] Chen Y, Chadderton L T, Gerald J F and Williams J S 1999 *Appl. Phys. Lett.* **74** 2960
[15] Balkas C M and Davis R F 1996 *J. Am. Ceram. Soc.* **79** 2309
[16] Ajayan P M 1997 *Carbon Nanotubes—Preparation and Properties* ed W E Thomas (Boca Raton: CRC)
[17] Ogino T and Aoki M 1979 *Oyo Buturi* (in Japanese) **48** 269
[18] Ogino T and Aoki M 1980 *Japan. J. Appl. Phys.* **19** 2395
[19] Goldstein A N, Echer C M and Alivisatos A P 1992 *Science* **256** 1425