

Synthesis and Characterization of Ga₂O₃ Nanobelts on Pt-Coated Substrates

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We have successfully grown gallium oxide (Ga₂O₃) nanobelts on a Pt-coated Si substrate by evaporating GaN powder at high temperature in the presence of nitrogen. The as-synthesized nanobelts with monoclinic structure were rectangular in cross-sectional shape and 20 – 1000 nm in width. Photoluminescence measurement under excitation at 325 nm showed that the Ga₂O₃ nanobelts had a blue emission at around 445 nm.

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I. INTRODUCTION

β -Ga₂O₃, a wide bandgap transparent conducting oxide material ($E_g = 4.9$ eV) [1], has been known for both conduction and luminescence properties [2]. Ga₂O₃ can be used as insulating oxide layer for all gallium-based semiconductors and has potential applications for optoelectronic devices in the deep-ultraviolet region. Also, Ga₂O₃ thin films are among the most promising materials for high-temperature gas sensors [3,4].

Since the first discovery of carbon nanotubes [5], nanoscale one-dimensional (1-D) materials have been of great interest due to their unique properties and promising applications in electrical, optical, and magnetic devices [6–13].

Accordingly, researchers have worked on the growth of Ga₂O₃ nanowires by various techniques [14–21]. Also, some researchers have prepared Ga₂O₃ nanobelts by thermally heating or evaporating Ga₂O₃ powder mixed with active carbon/carbon nanotubes [19] or with graphite [22], GaN powder [23], a mixture of Ga and Ga₂O₃ powders [24], a mixture of Ga and SiO₂ powders [25], and metallic Ga source [26]. Up to the present, various metals such as Au [27–31], Ir [32], Ni [33], and Fe [34] have been proved to play a catalytic role in synthesizing inorganic 1-D nanomaterials. As for Ga₂O₃ nanomaterials, nanowires have been produced by using a mixture of GaN and Ni/Co or Ni/Co/Y powders [14], Ga metal on Au-coated Si substrate [20], Au-coated GaAs material [17], GaN powder on In-coated sapphire substrate [21], and a mixture of GaN, graphite, and Ni powders [35].

Although carbon nanotubes have been synthesized by using platinum (Pt) catalyst [36–38], to our knowledge, synthesis of any inorganic nanomaterials, including Ga₂O₃, on Pt substrate has not been reported to date. In this paper, we report an approach in which we have

produced Ga₂O₃ nanobelts on Pt-coated Si substrates. We have employed thermal evaporation of GaN powder at a temperature of 900 °C. We have investigated the structural and photoluminescence (PL) properties of the as-prepared Ga₂O₃ nanobelts.

II. EXPERIMENTS

The synthesis was based on simple evaporation by using GaN powder as raw material and was carried out in a quartz tube (outer diameter: 75 mm, length: 50 cm) mounted vertically inside a high-temperature tube furnace [39]. The 99.99 %-pure GaN powders were placed on the lower holder at the center of a quartz tube. A layer of Pt (about 150 nm in thickness) was deposited on the SiO₂/Si substrate by a sputtering method. The substrate (15 × 15 mm side) covered with a Pt film was placed on the upper holder at a distance of about 5 mm from the GaN powders. The temperature was kept at 900 °C for 2 hours under a constant flow of nitrogen (N₂). N₂ was introduced into the quartz tube at the rate of 500 standard cubic centimeters per minute. The tube was then cooled naturally to room temperature in 8 h. The surface of the samples grown on substrates appeared with a white color after evaporation.

As-grown samples were investigated and analyzed by using glancing-angle (0.3°) X-ray diffraction (XRD, Xpert MPD-Philips with CuK1 radiation), scanning electron microscopy (SEM, Hitachi S-4200), transmission electron microscopy (TEM, Philips CM-200), and energy-dispersive X-ray spectroscopy (EDS) attached to the TEM. TEM samples were prepared by sonicating the substrate in acetone by ultrasonic treatment. A drop of the dispersion solution was then placed on a porous carbon film supported on a copper grid. The PL measurement was performed at room temperature by using a He-Cd laser line of 325 nm as the excitation source.

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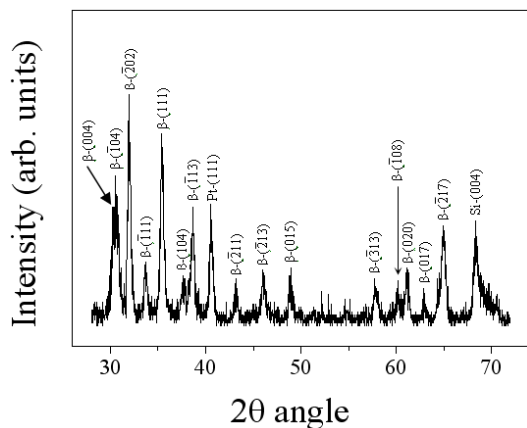


Fig. 1. X-ray diffraction patterns recorded from the Ga_2O_3 nanobelts.

III. RESULTS AND DISCUSSION

The experiment produced a wool-like array of nanomaterials covering the entire surface of the substrate. Figure 1 shows the typical XRD spectrum of the products. The reflection peaks can be readily indexed as (004), $(\bar{1}04)$, $(\bar{2}02)$, $(\bar{1}11)$, (111), (104), $(\bar{1}13)$, $(\bar{2}11)$, $(\bar{2}13)$, (015), $(\bar{3}13)$, $(\bar{1}08)$, (020), (017), and $(\bar{2}17)$ crystal planes of the crystalline monoclinic $\beta\text{-Ga}_2\text{O}_3$ structure, which is in good agreement with the reported data (JCPDS: 11-0370). The reflection peak at $2\theta = 69.20^\circ$ corresponds to the (004) reflection of the single-crystalline Si substrate. Also, the (111) diffraction peak of Pt from the substrate is detected.

Figure 2(a) is a side-view SEM image of the deposits on the surface of the substrate, indicating that the deposits are wool-like with a thickness of about $70\ \mu\text{m}$. Figure 2(b) is a typical high-magnification SEM image of the deposits, showing that the wool-like products consist of bunches of nanobelts. The waving and twist shapes of the nanobelts are apparent. For the nanobelts, the cross section is rectangular. Statistical analysis of many SEM images shows that the typical width is in the range of $20 - 1000\ \text{nm}$. Further analysis of the individual Ga_2O_3 nanobelts was performed by using TEM with EDS attached. EDS measurements indicated that the nanobelts consisted of the elements Ga and O, regardless of the position in the nanobelt (not shown here).

Figure 3(a) shows a TEM image of the products, indicating that each nanobelt has an almost uniform width along its entire length. We surmise that the darker-contrast parts apparent in some nanobelts are due to a twisting or bending effect. No spherical droplets or particles can be seen at the tips of these nanobelts. This observation suggests that the nanobelts may not grow by the conventional vapor-liquid-solid mechanism by a catalytic-assisted technique, in which a liquid metal droplet is located at the growth front of the wire and acts as the catalytic active site. Instead, Pt in this study

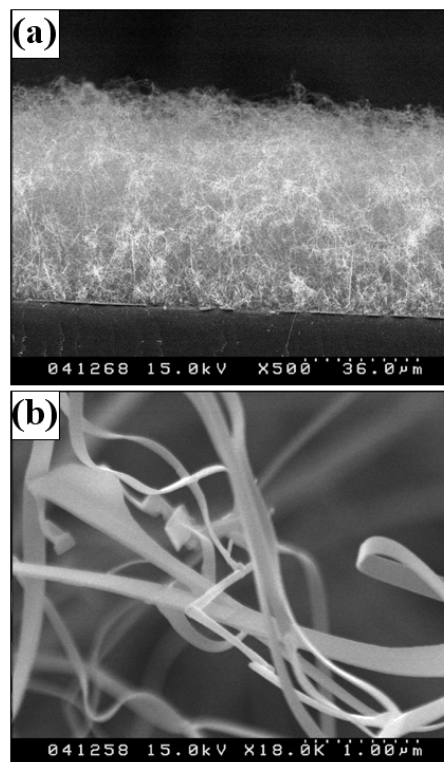


Fig. 2. (a) Side-view, and (b) high-magnification SEM images of the deposited nanobelts.

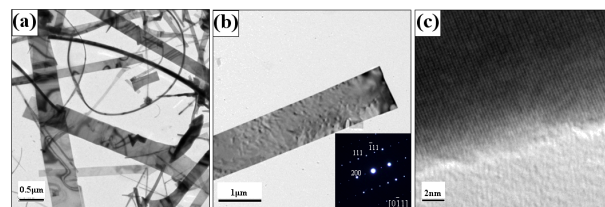


Fig. 3. (a) TEM image of the products. (b) TEM image of a single Ga_2O_3 nanobelt, and (c) HRTEM image.

may remain on the surface of the substrate during the entire process. Since we could not obtain recognizable or structurally uniform nanobelts in previous experiments by using the same synthesizing conditions with bare Si or SiO_2 substrates without Pt layers, we deduce that the formation of Ga_2O_3 nanobelts is promoted by the presence of Pt. Further study is necessary to reveal the exact role of Pt in the formation of Ga_2O_3 nanobelts.

Figure 3(b) shows a TEM image of a nanobelt with a width of $1000\ \text{nm}$. The corresponding SAED pattern in the inset of Figure 3(b) is recorded along the $[0\bar{1}1]$ zone axis, revealing that the Ga_2O_3 nanobelts display a monoclinic structure. Figure 3(c) is a typical high-resolution TEM (HRTEM) image of the nanobelt shown in Figure 3(b). The clear lattice fringes illustrate that the nanobelt is single-crystalline.

The PL of as-prepared Ga_2O_3 nanobelts was measured at room temperature. There is an apparent broad, strong

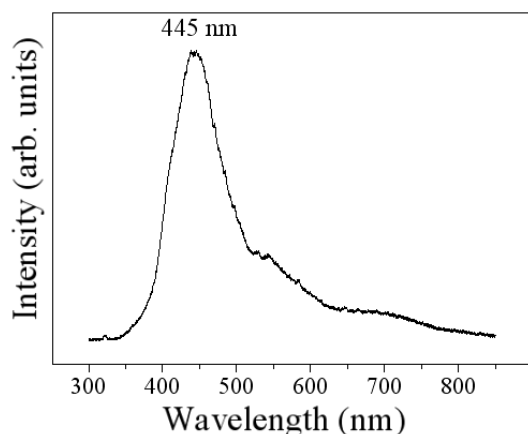


Fig. 4. Room-temperature PL spectrum of the Ga₂O₃ nanobelts with an excitation wavelength of 325 nm.

blue emission PL peak centered at about 445 nm, as shown in Figure 4. Binet and Gourier [2] suggested that this blue emission could be produced by recombination of an electron on a donor formed by oxygen vacancies with a hole on an acceptor which could be either gallium vacancies [40] or a gallium-oxygen vacancy pair [41]. We surmise that the above vacancies were easily generated in the present synthesis route at high temperature, supporting the origin of the blue emission. Although further systematic study is necessary in order to reveal the detailed mechanism of the observed emissions, Ga₂O₃ nanomaterials may have potential application in optoelectronic nanodevices, due to their possibilities of strong emission.

IV. CONCLUSION

In summary, we report the preparation of monoclinic Ga₂O₃ nanobelts on Pt-coated Si substrate by a thermal evaporation method of heating GaN powder at 900 °C under N₂ flow. The resulting Ga₂O₃ nanobelts are crystalline, with widths ranging from 20 to 1000 nm and lengths of several tens of micrometers. No Pt-containing nanoparticles are observed on the ends of the as-synthesized Ga₂O₃ nanobelts. The broad and strong PL emission band centered around 445 nm is observed at room temperature.

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REFERENCES

[1] H. H. Tippins, *Phys. Rev.* **140**, A316 (1965).

- [2] L. Binet and D. Gourier, *J. Phys. Chem. Solids* **59**, 1241 (1998).
- [3] M. Ogita, K. Higo, Y. Nakanishi and Y. Hatanaka, *Appl. Surf. Sci.* **175-176**, 721 (2001).
- [4] U. Hofer, J. Frank and M. Fleischer, *Sensors and Actuators B* **78**, 6 (2001).
- [5] S. Iijima, *Nature* **354**, 56 (1991).
- [6] E. W. Wong, P. E. Sheehan and C. M. Lieber, *Science* **277**, 1971 (1977).
- [7] J. T. Hu, T. W. Odom and C. M. Lieber, *Acc. Chem. Res.* **32**, 435 (1999).
- [8] Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science* **291**, 1947 (2001).
- [9] L. F. Dong, J. Jiao, D. W. Tuggle, J. Petty, S. A. Elliff and M. Coulter, *Appl. Phys. Lett.* **82**, 1096 (2003).
- [10] K. Bubke, H. Gnuwuch, M. Hempstead, J. Hammer and M. L. H. Green, *Appl. Phys. Lett.* **71**, 1906 (1997).
- [11] J. Y. Kim, H. W. Shim, E.-K. Suh, T. Y. Kim, S. H. Lee, Y. H. Mo and K. S. Nahm, *J. Korean Phys. Soc.* **44**, 137 (2004).
- [12] D.-H. Kim and H.-R. Lee, *J. Korean Phys. Soc.* **45**, 79 (2004).
- [13] H.-M. Kim, H. Lee, S. I. Kim, S. R. Ryu, T. W. Kang, D. Y. Kim, K. S. Chung, J. P. Hong and Y. D. Woo, *J. Korean Phys. Soc.* **45**, 701 (2004).
- [14] Y. C. Choi, W. S. Kim, Y. S. Park, S. M. Lee, D. J. Bae, Y. H. Lee, G. S. Park, W. B. Choi, N. S. Lee and J. M. Kim, *Adv. Mater.* **12**, 746 (2000).
- [15] H. Z. Zhang, Y. C. Kong, Y. Z. Wang, X. Du, Z. G. Bai, J. J. Wang, D. P. Yu, Y. Ding, Q. L. Hang and S. Q. Feng, *Solid State Commun.* **109**, 677 (1999).
- [16] B. C. Kim, K. T. Sun, K. S. Park, K. J. Im, T. Noh, M. Y. Sung and S. Kim, *Appl. Phys. Lett.* **80**, 479 (2002).
- [17] C. H. Liang, G. W. Meng, G. Z. Wang, Y. W. Wang, L. D. Zhang and S. Y. Zhang, *Appl. Phys. Lett.* **78**, 3202 (2001).
- [18] X. C. Wu, W. H. Song, W. D. Huang, M. H. Pu, B. Zhao, Y. P. Sun and J. J. Du, *Chem. Phys. Lett.* **328**, 5 (2000).
- [19] G. Gundiah, A. Govindaraj and C. N. R. Rao, *Chem. Phys. Lett.* **351**, 189 (2002).
- [20] P. Guha, S. Chakrabarti and S. Chaudhuri, *Physica E* **23**, 81 (2004).
- [21] J. Zhang and F. Jiang, *Chem. Phys.* **289**, 243 (2003).
- [22] J. Zhang and L. D. Zhang, *Solid State Commun.* **122**, 493 (2002).
- [23] Z. R. Dai, Z. W. Pan and Z. L. Wang, *J. Phys. Chem. B* **106**, 902 (2002).
- [24] J. Zhang, F. Jiang and L. D. Zhang, *Phys. Lett. A* **322**, 363 (2004).
- [25] B. Y. Geng, L. D. Zhang, G. W. Meng, T. Xie, X. S. Peng and Y. Lin, *J. Cryst. Growth* **259**, 291 (2003).
- [26] X. Xiang, C.-B. Cao, Y.-J. Guo and H.-S. Zhu, *Chem. Phys. Lett.* **378**, 660 (2003).
- [27] L. F. Dong, J. Jiao, M. Coulter and L. Love, *Chem. Phys. Lett.* **376**, 653 (2003).
- [28] N. Sakulchaicharoen and D. E. Resasco, *Chem. Phys. Lett.* **377**, 377 (2003).
- [29] Y. W. Wang, L. D. Zhang, C. H. Liang, G. Z. Wang and X. S. Peng, *Chem. Phys. Lett.* **357**, 314 (2002).
- [30] H. J. Yuan, S. S. Xie, D. F. Liu, X. Q. Yan, Z. P. Zhou, L. J. Ci, J. X. Wang, Y. Gao, L. Song, L. F. Liu, W. Y. Zhou and G. Wang, *Chem. Phys. Lett.* **371**, 337 (2003).

- [31] X. B. Zeng, Y. Y. Xu, S. B. Zhang, Z. H. Hu, H. W. Diao, Y. Q. Wang, G. L. Kong and X. B. Jiao, *J. Cryst. Growth* **247**, 13 (2003).
- [32] H. W. Kim and N. H. Kim, *Appl. Phys. A* **80**, 537 (2005).
- [33] T. Y. Kim, S. H. Lee, Y. H. Mo, H. W. Shim, K. S. Nahm, E.-K. Suh, J. W. Yang, K. Y. Lim and G. S. Park, *J. Cryst. Growth* **257**, 97 (2003).
- [34] S. S. Fan, J. Cao, H. Y. Dang, Q. Gu and J. H. Zhao, *Mater. Sci. Eng. C* **15**, 295 (2001).
- [35] W. Q. Han, P. Kohler-Redlich, F. Ernst and M. Rühle, *Solid State Commun.* **115**, 527 (2000).
- [36] M. Yudasaka, Y. Kasuya, F. Kokai, K. Takahashi, M. Takizawa, S. Bandow and S. Iijima, *Appl. Phys. A* **74**, 377 (2002).
- [37] C. J. Lee, J. Park, J. M. Kim, Y. Huh, J. Y. Lee and K. S. No, *Chem. Phys. Lett.* **327**, 277 (2000).
- [38] Y. Saito, K. Nishikubo, K. Kawabata and T. Matsumoto, *J. Appl. Phys.* **80**, 3062 (1996).
- [39] N. H. Kim and H. W. Kim, *Appl. Surf. Sci.* **242**, 29 (2005).
- [40] T. Harwig and F. Kellendouk, *J. Solid State Chem.* **24**, 255 (1978).
- [41] V. I. Vasil'tsiv, Ya. M. Zakharko and Ya. I. Prim, *Ukr. Fiz. Zh.* **33**, 1320 (1988).