

Amorphous gallium oxide nanowires synthesized by metalorganic chemical vapor deposition

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Abstract

We have prepared the large-scaled gallium oxide nanowire arrays on sapphire substrates using a reaction of a trimethylgallium (TMGa) and oxygen (O₂) mixture. The cross-section of the gallium oxide nanowires had a circular shape with the diameter of about 40–110 nm. Transmission electron microscopy and X-ray diffraction analysis together showed that the nanowires were amorphous phase. Photoluminescence measurements indicated that as-prepared nanowires showed two emission band at 365 and 470 nm.

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1. Introduction

In recent years, the preparation of one-dimensional nanomaterials has drawn intensive interests due to their novel physical properties and potential applications in nanoscale electronic and optoelectronic devices [1–7]. To date, several kinds of binary oxide materials such as MgO, SiO₂, In₂O₃, GeO₂, ZnO, and NiO were synthesized as nanowires [8–15]. As one of the most important binary oxide nanowires with a wide bandgap of 4.9 eV [16], gallium oxide nanowires have great potential application in optoelectronic nanodevices and gas sensors [17,18].

Although many researchers have prepared gallium oxide nanowires by various methods such as using a physical evaporation of Ga powders [19], using dc arc discharge of GaN powders with a transition metal catalyst [20], thermal annealing of milled GaN powders [21], heating a composite material of GaAs and Au [22], and using a reaction with a mixture of Ga₂O₃ powder and graphite [23] or with a mixture of Ga₂O₃ powder and active carbon/carbon nanotubes [24], there are rare reports on the synthesis of gallium oxide nanowires using the metalorganic chemical vapor deposition (MOCVD) method.

In the present work, we report on the synthesis of gallium oxide nanowires on sapphire substrates without employing a catalyst using a simple reaction of a trimethylgallium (TMGa) and oxygen (O₂) mixture, at a temperature of 600 °C. We have characterized the obtained samples with scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), and photoluminescence (PL) spectroscopy.

2. Experimental

Fig. 1 shows a schematic representation of the MOCVD system used to grow gallium oxide nanowires. The vertical reactor was made of stainless steel, and has been cooled by water. A lamp heated the graphite susceptor to a certain growth temperature. We chose the (0001)-oriented sapphire (α -Al₂O₃) as a substrate material. Before inserting into the chamber, the substrate was chemically cleaned with acetone (CH₃COCH₃) and water. In the growth process, we have used TMGa and oxygen (O₂), respectively, as the gallium and oxygen sources. The Ar as a carrier gas flowed through the TMGa bubbler maintained at –5 °C, with the flow rate of 30 standard cubic centimeters per minute (sccm). The flow rate of O₂ was set to 6 sccm. The reaction temperature was 600 °C with a deposition time of 5 min.

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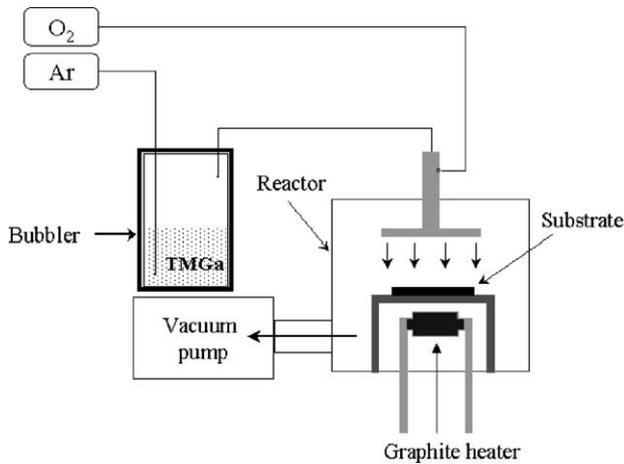


Fig. 1. Schematic illustration of the MOCVD system.

Structural property was assessed by XRD (Philips CM20T) with Cu $K\alpha_1$ radiation ($\lambda = 0.154056$ nm), SEM (Hitachi S-4200) operated at 15 kV with energy-dispersive X-ray spectroscopy (EDS) installed, and TEM (Philips CM-200) operated at 200 kV. The TEM sample was prepared by dispersing the powder in alcohol. Imaging was enabled by dispersing few drops of suspension onto carbon coated copper grid. In order to investigate the luminescence properties, PL was carried out at room temperature, with a Shimadzu fluorescence spectrophotometer (RF-5301PC). The excitation light was the monochromatic light from a xenon short arc lamp with a wavelength of $\lambda = 250$ nm.

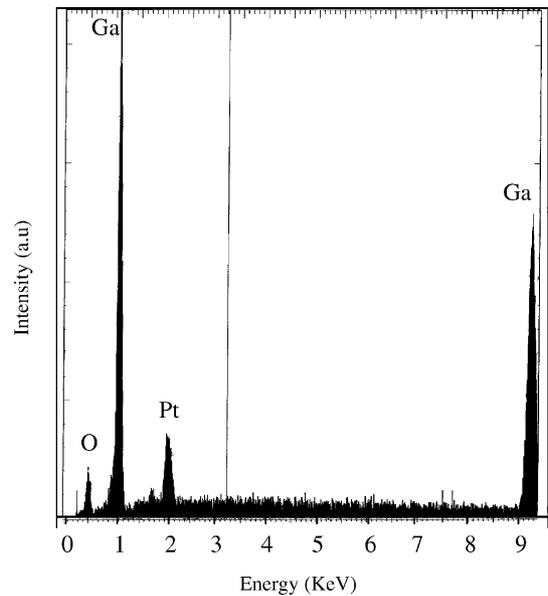


Fig. 3. The EDS spectrum showing the chemical compositions of the nanowires.

3. Results and discussion

Statistical analysis of many SEM images shows that the deposits have diameters ranging from 40 to 110 nm. Fig. 2a shows a typical SEM image of the deposits on the surface of the sapphire substrate, revealing that the wire-like nanostructures are slightly curved with uniform diameter along the growth direction. Fig. 2b shows the lower magnifica-

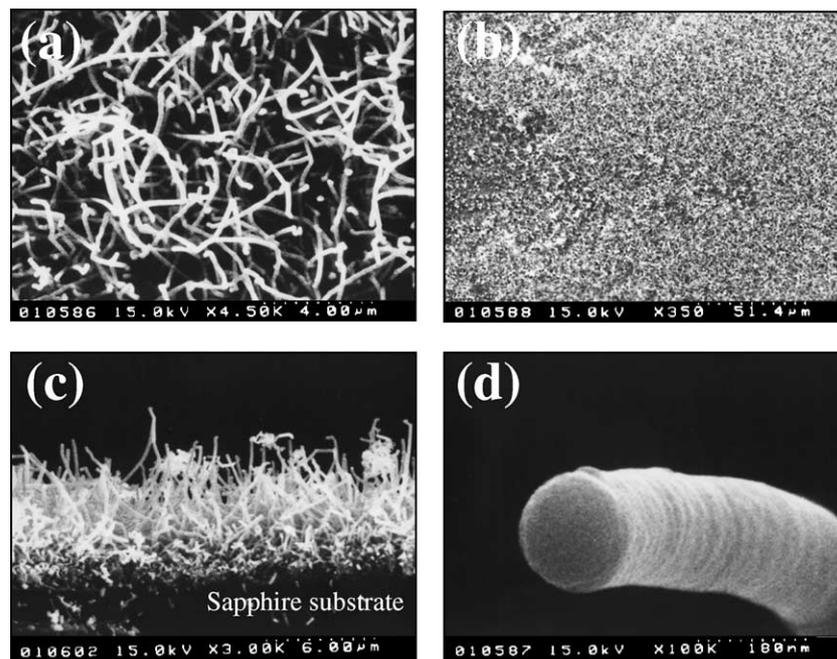


Fig. 2. SEM images of gallium oxide nanowires. (a) Plan-view image. (b) A lower magnification plan-view image showing the uniform distribution of nanowires over a large area. (c) Side view image. (d) High-magnification image of a nanowire.

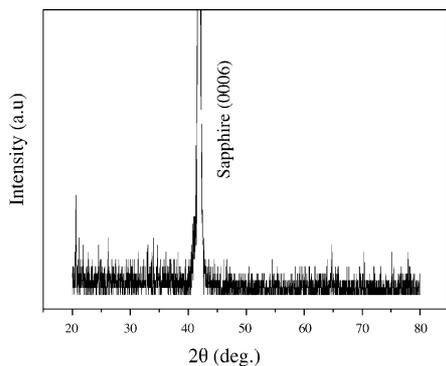


Fig. 4. X-ray diffraction pattern recorded from gallium oxide nanowires.

tion SEM image showing that the nanowires have a uniform distribution over a large area. Fig. 2c shows the SEM image of the side view of the nanowires, indicating that the growth direction of the nanowires is randomized and the lengths of the nanowires are in the range of several micrometers. Fig. 2d shows the high-magnification SEM image of a nanowire, revealing that the cross-section of the stem of the nanowire has a circular shape with no nanoparticle at its tip. The nanowires are gallium oxide, as shown by the typical EDS spectrum collected from the nanowires (Fig. 3). The spectrum clearly identifies the peaks of Ga, O, and Pt. Since the Pt-related peak is due to the preparation of SEM specimens, the spectrum indicates that the components of the nanowires are only Ga and O.

Fig. 4 shows the XRD patterns of the gallium oxide nanowires on sapphire substrates, revealing that the nanowires are fully amorphous. No reflections are clearly discerned other than the Al_2O_3 (0006) peak from the substrate. We have observed the morphology of the gallium oxide nanowires by TEM. Fig. 5a shows the low magnification TEM image of the nanowires, indicating that the nanowires display the wire-like shape with diameters of 50–90 nm, and no spherical droplets can be seen at tips of these nanowires, agreeing with SEM images. Fig. 5b shows the high resolution TEM (HRTEM) image with the corresponding SAED pattern. Since there are no lattice fringes inside the nanowires and they have the highly diffusive SAED ring pattern, the HRTEM image and electron diffraction coincidentally identify that they are of amorphous nature.

Since no catalysts were intentionally used for the growth of our nanowires and no nanoparticles or impurities are clearly observed on the tips of prepared nanowires, we surmise that the growth of gallium oxide nanowire is a self-catalytic process and is not dominated by the VLS mechanism, in which a metal particle as a catalytic site is located at the growth front of the wire [25]. Further systematic study is underway to derive the exact mechanism for the formation of gallium oxide nanowires by the MOCVD method.

The as-prepared gallium oxide nanowires show strong emission at room temperature, as shown in Fig. 6. The PL spectrum of gallium oxide nanowires presents two emission bands around 365 nm (3.405 eV) and 470 nm (2.645 eV)

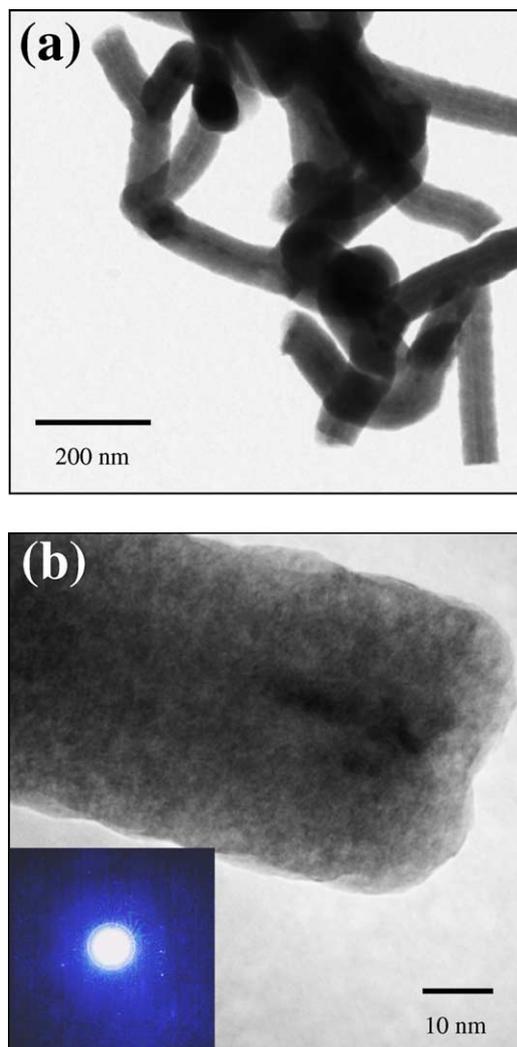


Fig. 5. TEM characterization of the gallium oxide nanowires. (a) Low magnification TEM image. (b) High resolution TEM image (inset: corresponding electron diffraction pattern).

when excited at 250 nm. The emission at 365 nm is relatively weak comparing with that at 470 nm. The weak emission band around 365 nm is in the ultraviolet (UV) spectral region. UV luminescence in Ga_2O_3 has been reported to be

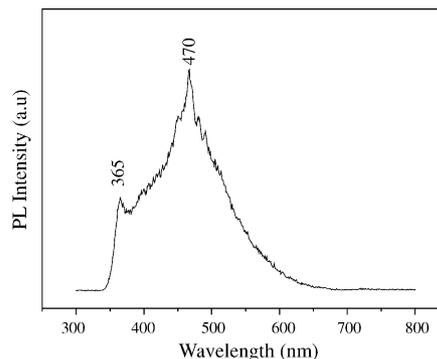


Fig. 6. Photoluminescence spectrum of gallium oxide nanowires with an excitation wavelength at 250 nm.

attributed to an intrinsic transition, due to the recombination of a self-trapped exciton [26]. The broad and strong blue or blue-green emission at about 470 nm is associated with the vacancies in Ga₂O₃ [27,28]. Our previous experiments indicated that the gallium oxide materials prepared on different substrates, such as Si(100) and SiO₂, also present two emission bands around 365 and 470 nm, revealing that the emission peaks around 365 and 470 nm in Fig. 6 are not from the sapphire substrates. Although further systematic study is necessary in order to reveal the mechanism of the observed emissions, gallium oxide nanowires may have potential application in optoelectronic nanodevices due to their possibilities of strong emission.

4. Conclusion

We have demonstrated the growth of gallium oxide nanowires on sapphire substrate using the MOCVD technique. SEM and TEM confirm that the average diameter of gallium oxide nanowires obtained by this method ranges from 40 to 110 nm with no nanoparticles at their tips. The as-prepared gallium oxide nanowires are of amorphous nature. The PL of the nanowires shows a weak emission band at 365 nm and a broad and strong emission band around 470 nm.

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References

- [1] B.I. Yakobson, R.E. Smalley, *Am. Sci.* 85 (1997) 324.
- [2] J.T. Hu, T.W. Odom, C.M. Lieber, *Acc. Chem. Res.* 32 (1999) 435.
- [3] L.F. Dong, J. Jiao, D.W. Tuggle, J. Petty, S.A. Elliff, M. Coulter, *Appl. Phys. Lett.* 82 (2003) 1096.
- [4] Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* 291 (2001) 1947.
- [5] M. Law, H. Kind, F. Kim, B. Messer, P. Yang, *Angew. Chem.* 41 (2002) 2405.
- [6] A.P. Alivisatos, *Science* 271 (1996) 933.
- [7] E.W. Wong, P.E. Sheehan, C.M. Lieber, *Science* 277 (1997) 1971.
- [8] P. Yang, C.M. Lieber, *Science* 273 (1996) 1836.
- [9] P. Yang, C.M. Lieber, *J. Mater. Res.* 12 (1997) 2981.
- [10] Z.L. Wang, R.P. Gao, J.L. Gole, J.D. Stout, *Adv. Mater.* 12 (2000) 1938.
- [11] Y.Q. Zhu, W.B. Hu, W.K. Hsu, M. Terrones, N. Grobert, J.P. Hare, H.W. Kroto, D.R.M. Walton, H. Terrones, *J. Mater. Chem.* 9 (1999) 3173.
- [12] C.H. Liang, G.W. Meng, Y. Lei, F. Philipp, L.D. Zhang, *Adv. Mater.* 13 (2001) 1330.
- [13] Z.G. Bai, D.P. Yu, H.Z. Zhang, Y. Ding, X.Z. Gai, Q.L. Hang, G.C. Xiong, S.Q. Feng, *Chem. Phys. Lett.* 303 (1999) 311.
- [14] M.H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, P. Yang, *Adv. Mater.* 13 (2001) 113.
- [15] Y. Zhan, C. Zheng, Y. Liu, G. Wang, *Mater. Lett.* 57 (2003) 3265.
- [16] H.H. Tippins, *Phys. Rev.* 140 (1965) A316.
- [17] D.S. Ginly, C. Bright, *Mater. Res. Soc. Bull.* 25 (2000) 15.
- [18] N. Yamazoe, *Sens. Actuators B* 5 (1991) 7.
- [19] 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, S.Q. Feng, *Solid State Commun.* 109 (1999) 677.
- [20] 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, J.M. Kim, *Adv. Mater.* 12 (2000) 746.
- [21] B.C. Kim, K.T. Sun, K.S. Park, K.J. Im, T. Noh, M.Y. Sung, S. Kim, *Appl. Phys. Lett.* 80 (2002) 479.
- [22] C.H. Liang, G.W. Meng, G.Z. Wang, Y.W. Wang, L.D. Zhang, S.Y. Zhang, *Appl. Phys. Lett.* 89 (2001) 3202.
- [23] X.C. Wu, W.H. Song, W.D. Huang, M.H. Pu, B. Zhao, Y.P. Sun, J.J. Du, *Chem. Phys. Lett.* 328 (2000) 5.
- [24] G. Gundiah, A. Govindaraj, C.N.R. Rao, *Chem. Phys. Lett.* 351 (2002) 189.
- [25] J. Zhang, F. Jiang, *Chem. Phys.* 289 (2003) 243.
- [26] E.G. Villora, K. Hatanaka, H. Odaka, T. Sugawara, T. Miura, H. Fukumura, T. Fukuda, *Solid State Commun.* 127 (2003) 385.
- [27] T. Harwig, G.J. Wubs, G.J. Dirksen, *Solid State Commun.* 18 (1976) 1223.
- [28] Q.P. Wang, D.H. Zhang, H.L. Ma, X.H. Zhang, X.J. Zhang, *Appl. Surf. Sci.* 220 (2003) 12.