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Formation of amorphous and crystalline gallium oxide nanowires by metalorganic chemical vapor deposition

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Abstract

We have synthesized the large-scaled gallium oxide nanowire arrays using a reaction of a trimethylgallium (TMGa) and oxygen (O_2) mixture. Scanning electron microscopy revealed that the cross-section of the nanowires had a circular shape with the diameter of about 50–150 nm and the length up to several tens of micrometers. High-resolution transmission electron microscopy showed that the gallium oxide nanowires were of amorphous or polycrystalline nature.

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Keywords: MOCVD; Gallium oxide; Nanowires

1. Introduction

One-dimensional (1D) nanostructures such as nanotubes, nanowires, and nanobelts are of great interest for their novel physical properties and potential applications in nanoscale electronic and optoelectronic devices [1–7]. Recently, much attention has been paid to the nanowires [8–14] and nanobelts [15] of the family of oxides and the synthesis of several binary oxide nanowires such as MgO [8,9], SiO_2 [10,11], In_2O_3 [12], GeO_2 [13], and ZnO [14] has been reported. As a wide bandgap ($E_g = 4.9$ eV) compound [16], nanometer-scale gallium oxide with large surface area/volume ratio is supposed to exhibit particular conduction and optical properties [17] and thus has great potential application in optoelectronic nanodevices and gas sensors [18,19].

Gallium oxide nanowires have been successfully synthesized by using a physical evaporation of Ga powders [20], using dc arc discharge of GaN powders with a transition metal catalyst [21], thermal annealing of milled GaN powders [22], heating a composite material of GaAs and Au [23], and using a reaction with a mixture of Ga_2O_3 powder and graphite [24] or with a mixture of Ga_2O_3 powder and carbon nanotubes [25]. However, to our knowledge, synthesis of gallium oxide nanowires using the metalorganic chemical vapor deposition (MOCVD) method has not been reported to date.

In this communication, we demonstrate the production of the gallium oxide nanowires on Si substrates without employing a catalyst using a simple reaction of a trimethylgallium (TMGa) and oxygen (O_2) mixture, at a temperature of 550 °C. We prepared the

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nanowires by controlling the gas flow ratio. We investigated the structural morphologies of gallium oxide nanowires using plan-view and cross-sectional scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and transmission electron microscopy (TEM).

2. Experimental

A schematic illustration of the MOCVD reactor used in our experiments is described in Fig. 1. Immediately prior to deposition, the p-type Si substrate with (1 0 0) orientation was cleaned with organic solvents and dried. TMGa and O_2 were used as the Ga and O sources with purified Ar as the carrier gas. The temperature of the TMGa bubbler was fixed at −5 °C. Mass flow controllers separately controlled the flow of Ar and O_2 gases and the gas flow ratio of Ar to O_2 was in the range of 1–5. The Ar gas flow rate was fixed at 30 standard cubic centimeters per minute (sccm) and the O_2 gas flow rate was varied

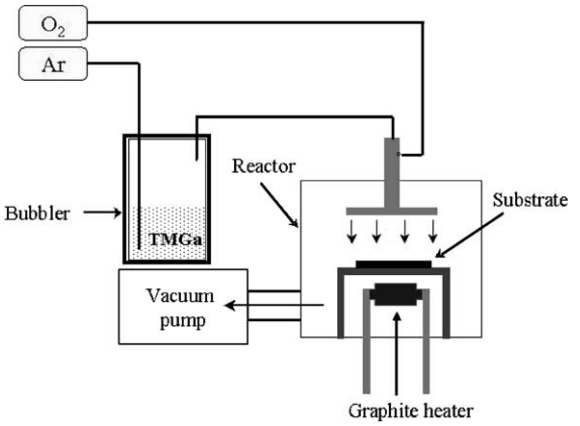

Fig. 1. Schematic illustration of the MOCVD reactor.

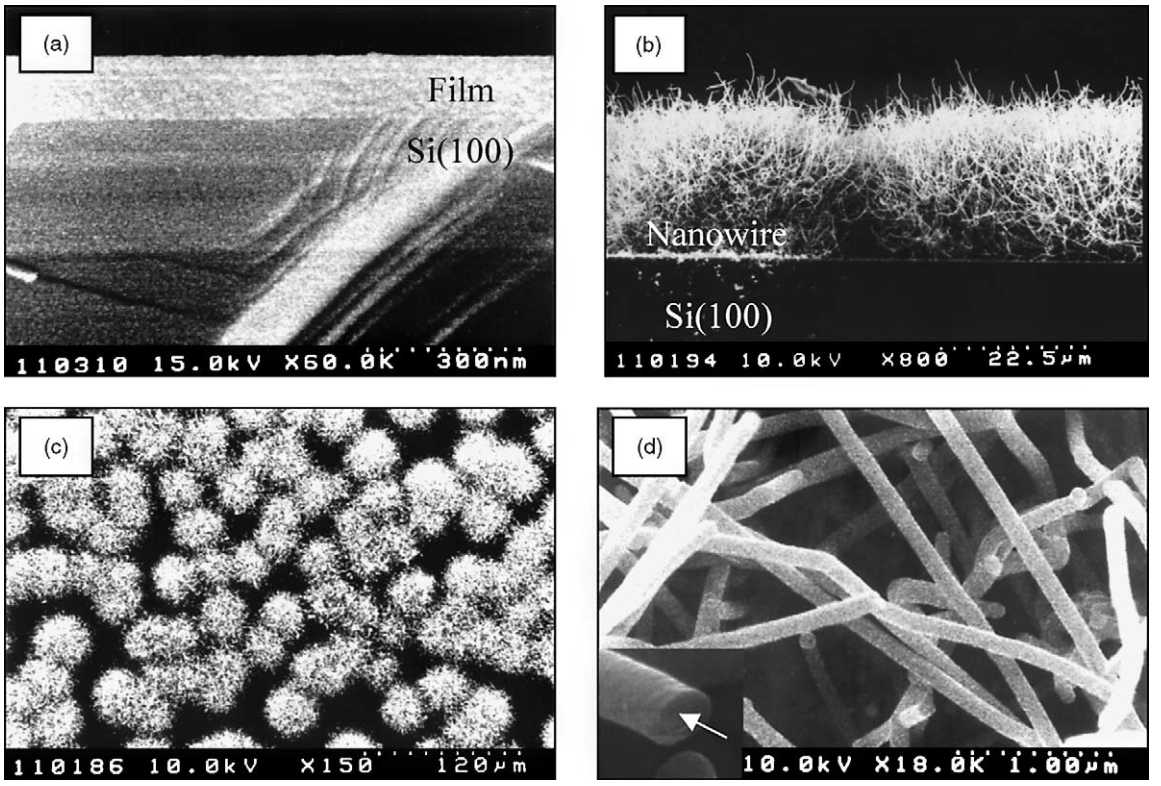

Fig. 2. SEM images of gallium oxide deposits grown on Si(1 0 0) substrate when the Ar/O_2 gas flow ratios are (a) 3 and (b)–(d) 5. (b) Cross-sectional image; (c) plain-view image; (d) high-magnification images (inset: magnified image of a deposit, exhibiting the circular cross-section).

between 6 and 30 sccm. The deposition time and temperature, respectively, were approximately 5 min and 550 °C.

XRD patterns were recorded on a Philips CM20T diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 0.154056$ nm). SEM was carried out with a Hitachi S-4200 microscope operated at 30 keV. TEM was carried out with a Philips CM-200 microscope operated at 200 kV with energy-dispersive X-ray spectroscopy (EDS) attached. TEM specimens were prepared by dispersing the powder in alcohol by ultrasonic treatment, dropping onto a porous carbon film supported on a copper grid, and then air-dried.

3. Results and discussion

The film structure and the 1D nanostructure are generated, respectively, with the Ar/O_2 gas flow ratio of 1–3 and 5, indicating that the Ar/O_2 gas flow ratio affects the morphology of the deposits. Fig. 2a and b shows the SEM images of the deposits when the Ar/O_2 gas flow ratios are 3 and 5, respectively. The large amounts of 1D deposits are formed having relatively uniform diameters in the range of 50–150 nm and the products are accumulated on most surfaces inside the chamber. The plain-view SEM image of the 1D deposits (Fig. 2c) show that this raw material has a wool-like shape, consisting of bundled aggregates of 1D deposits. Fig. 2d is the high-magnification SEM image of the 1D deposits, revealing that the deposits are relatively straight and slightly curved with uniform diameter along the growth direction. Close examination of the image reveals that the cross-section of the stem of the 1D deposit has a circular shape. By increasing the Ar/O_2 gas flow ratio (higher than 5), we obtained the nanowires with smaller diameters, indicating that the relative amounts of Ga and O atoms affect the diameter of the nanowires.

In order to investigate the crystallinity of 1D deposits grown on Si substrates, we performed an XRD analysis. Fig. 3 shows the XRD spectrum of the 1D deposit grown at 550 °C. A strong Ga_2O_3 diffraction peak is not found and instead broad peaks with 2θ around 35° and 63° are detected, implying the presence of an amorphous phase. However, weak diffraction peaks were observed and the positions of the peaks are in good agreement with $(\bar{1}\,0\,4)$ or $(\bar{2}\,0\,2)$,

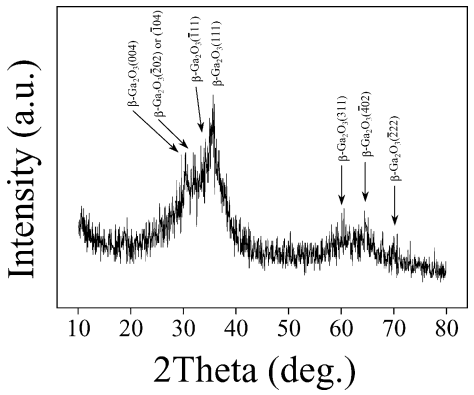

Fig. 3. X-ray diffraction patterns recorded from 1D gallium oxide deposits.

$(\bar{1}\,1\,1)$, $(3\,1\,1)$, $(\bar{4}\,0\,2)$ and $(\bar{2}\,2\,2)$ of β-Ga_2O_3 (JCPDS card: No. 11-370). XRD data indicate that the deposits are crystallographically amorphous or contain very small crystallites with a β-Ga_2O_3 phase.

We performed a TEM analysis for further characterization of the microstructures of the 1D deposits. The typical EDS spectrum collected from the 1D deposit is depicted in Fig. 4. The spectrum clearly identifies the peaks of Ga and O indicating the

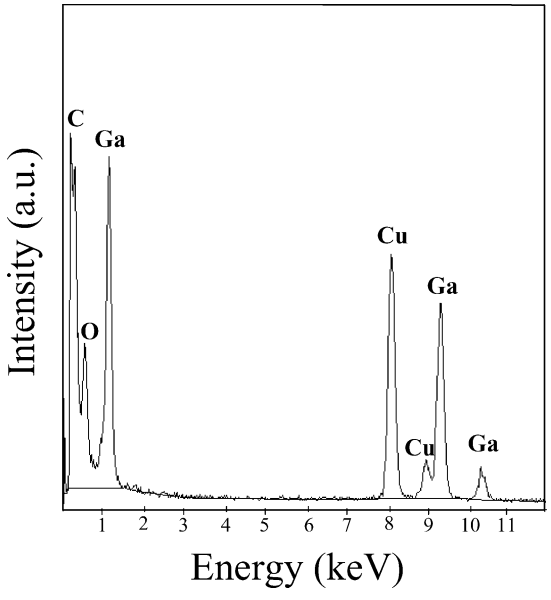

Fig. 4. A typical EDS spectrum of the 1D gallium oxide deposits grown on Si(1 0 0) substrate. The Cu and C peaks come from the supporting carbon-coated copper grids in TEM sample preparation.

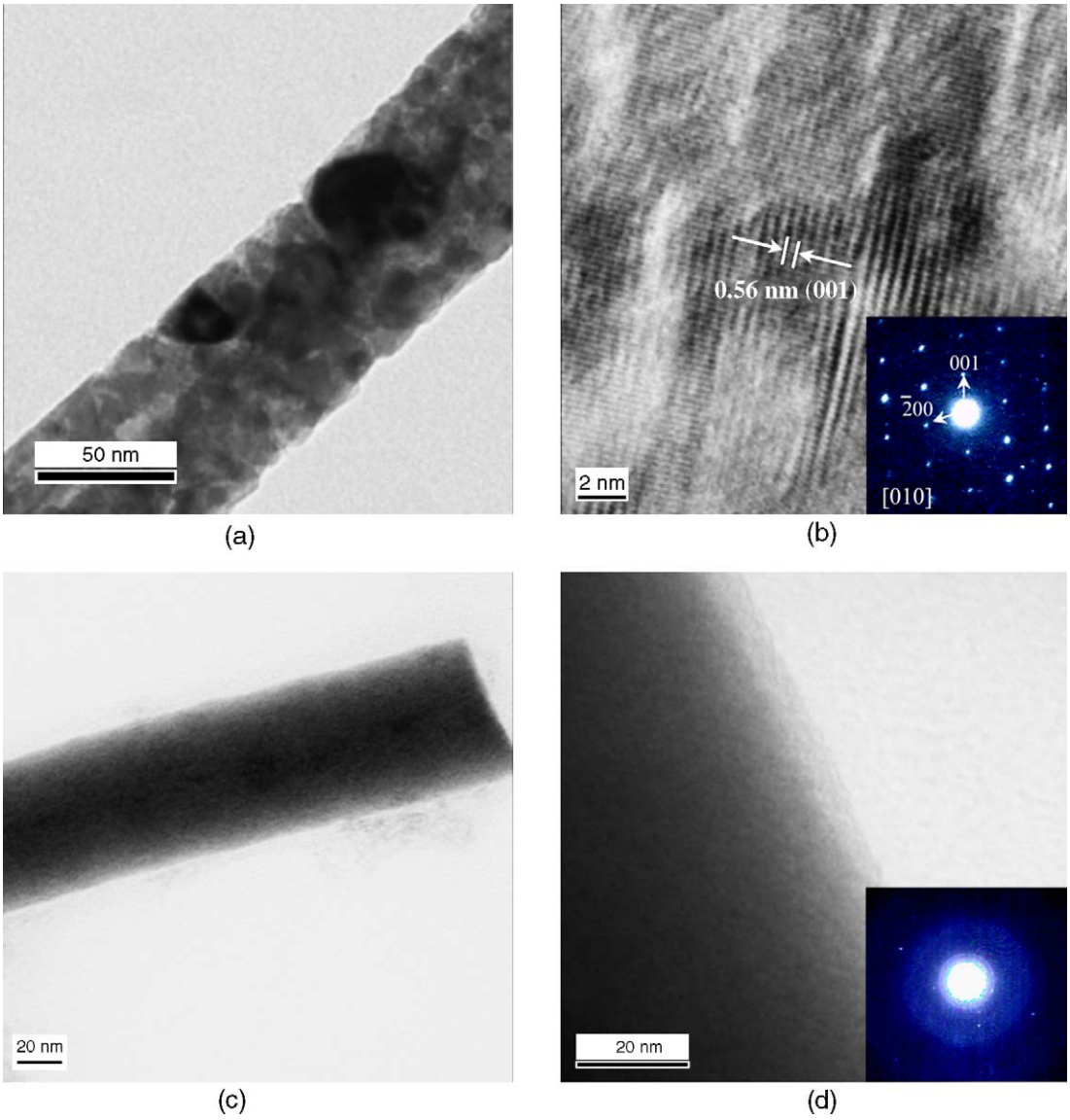

Fig. 5. TEM characterization of the gallium oxide nanowires with a (a, b) rough and (c, d) smooth surface. (a, c) Low magnification TEM image; (b, d) high resolution TEM image (inset: corresponding electron diffraction pattern).

formation of gallium oxide. The C and Cu-related peaks are due to the contamination from the carbon-coated copper grids while preparing TEM specimens, indicating that the components of the 1D deposits are only Ga and O.

TEM studies have revealed that the 1D deposits can be categorized into two distinct types of nanowires: nanowires with smooth surfaces and nanowires with rough surfaces. Fig. 5a shows the typical TEM image of the gallium oxide nanowires with rough surfaces, indicating that the nanowires are in the form of a solid rod. Fig. 5b shows the high resolution TEM (HRTEM) image of a gallium oxide nanowire with a rough surface, revealing the visible lattice fringes. The interplanar spacing is about 0.56 nm, corresponding to the (0 0 0 1) planes of monoclinic β-Ga_2O_3. The corresponding selected area electron diffraction (SAED) pattern with a [0 1 0] zone axis also reveals that the

nanowires are monoclinic β-Ga_2O_3. However, the high resolution TEM images taken from different parts of the nanowire show the different orientation of lattice planes, revealing the polycrystalline nature of the material.

Fig. 5c shows the typical TEM image of the gallium oxide nanowires with smooth surfaces, confirming that the nanowires are in the form of a solid rod. Fig. 5d shows the HRTEM image with the corresponding SAED pattern. The HRTEM image and electron diffraction coincidentally identify that they are of an amorphous nature. Although it is not clear how to control the crystallinity of the nanowire, we expect that employing the metal catalyst promotes the reaction of Ga and O atoms, helping to grow more crystalline nanowires. Further study is underway.

No nanoparticles or impurities have been observed at the end of the gallium oxide nanowire in this synthesis route. Compared with other synthetic procedures of the gallium oxide nanowires, we emphasize the fact that no catalysts were intentionally used for the growth of our nanowires. Since no nanoparticles or impurities are clearly observed on the prepared nanowires, we surmise that the growth of gallium oxide nanowire is a self-catalytic growth. Intensive investigation is required to derive the exact mechanism for the formation of gallium oxide nanowires reported in the present work.

4. Conclusion

In summary, we have described the growth of gallium oxide nanowires in bulk quantities directly on the Si substrate at a temperature of 550 °C using the MOCVD technique. The morphology of the deposits changes from the film structure to the 1D nanostructure by increasing the Ar/O_2 gas flow ratio. We have investigated the structural natures of the gallium oxide nanowires by SEM, XRD, and TEM. The as-synthesized gallium oxide nanowires are amorphous or polycrystalline, having diameters of 50–150 nm, lengths of several tens of micrometers. The current process represents a valuable approach for preparing gallium oxide nanowires in high yield using the conventional TMGa as precursor.

Acknowledgements

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