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The growth of ultralong and highly blue luminescent gallium oxide nanowires and nanobelts, and direct horizontal nanowire growth on substrates

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Abstract

We report the growth of ultralong $\beta$-Ga$_2$O$_3$ nanowires and nanobelts on silicon substrates using a vapor phase transport method. The growth was carried out in a tube furnace, with gallium metal serving as the gallium source. The nanowires and nanobelts can grow to lengths of hundreds of nanometers and even millimeters. Their full lengths have been captured by both scanning electron microscope (SEM) and optical images. X-ray diffraction (XRD) patterns and transmission electron microscope (TEM) images have been used to study the crystal structures of these nanowires and nanobelts. Strong blue emission from these ultralong nanostructures can be readily observed by irradiation with an ultraviolet (UV) lamp. Diffuse reflectance spectroscopy measurements gave a band gap of 4.56 eV for these nanostructures. The blue emission shows a band maximum at 470 nm. Interestingly, by annealing the silicon substrates in an oxygen atmosphere to form a thick SiO$_2$ film, and growing Ga$_2$O$_3$ nanowires over the sputtered gold patterned regions, horizontal Ga$_2$O$_3$ nanowire growth in the non-gold-coated regions can be observed. These horizontal nanowires can grow to as long as over 10 $\mu$m in length. Their composition has been confirmed by TEM characterization. This represents one of the first examples of direct horizontal growth of oxide nanowires on substrates.

Supplementary data are available from stacks.iop.org/Nano/19/155604

1. Introduction

Monoclinic gallium oxide ($\beta$-Ga$_2$O$_3$) is a wide band gap material ($E_g \approx 4.9$ eV), and it exhibits blue luminescence [1]. For the examination of the electrical, optical, and chemical sensing properties of Ga$_2$O$_3$ nanostructures, several approaches have been employed to grow various one-dimensional (1D) Ga$_2$O$_3$ nanostructures such as nanowires, nanorods, nanobelts/nanoribbons, and nanotubes [2–14]. Among these, Ga$_2$O$_3$ nanowires have been synthesized via catalyst-assisted growth [2–5, 13], direct thermal evaporation (using Ga$_2$O$_3$, Ga, or GaN powder) [6–9, 14], and the microwave plasma reaction method [10]. Electrical property measurements of Ga$_2$O$_3$ nanowires and nanoribbons have revealed n-type semiconductor behavior [2, 6], and p-type behavior upon doping with zinc [15]. Electrical responses of Ga$_2$O$_3$ nanowires upon exposure to trace amounts of NH$_3$ and NO$_2$ gases have been detected [2]. A sharp increase in field emission intensity above the threshold field has been recorded for Ga$_2$O$_3$–C nanocables [9]. Fast photocurrent responses have also been measured for Ga$_2$O$_3$ nanowires [5]. Certainly many studies have shown that these 1D Ga$_2$O$_3$ nanostructures give blue photoluminescence with emission band maxima in the 400–500 nm range. The continuous exploration of the synthesis of high-quality Ga$_2$O$_3$ nanowires and the examination of their various properties should provide better assessment of their advantages for specific areas of application, as compared to other oxide nanowire systems. Despite the reported observation of strong blue photoluminescence from Ga$_2$O$_3$ nanowires, no direct...
optical images of the blue light emission from these nanowires have been presented. Furthermore, although exceptionally long 1D Ga$_2$O$_3$ nanostructures grown to several hundreds of microns, and even on the order of millimeters, have been reported, no electron microscopic images have been provided to show their fully extended lengths [8, 13]. In fact, growth of ultralong Ga$_2$O$_3$ nanowires and nanobelts to such lengths is rare. More typically, the nanowires have lengths on the order of several microns to tens of microns. The ability to grow relatively straight Ga$_2$O$_3$ nanowires and nanobelts to hundreds of microns or a few millimeters in length should greatly facilitate their fabrication into devices for the measurements of physical properties, including chemical sensing performance and catalytic properties [16]. In this study, we have successfully grown ultralong Ga$_2$O$_3$ nanowires and nanobelts with lengths on the order of sub-millimeters to millimeters using a gold-catalyzed vapor deposition method at 750 °C. SEM and optical images of the full lengths of these ultralong nanowires and nanobelts on silicon substrates are provided here. Their strong blue emission can be directly observed. The crystal structure and optical property characterization of these nanowires and nanobelts are also presented.

Another interesting aspect of this study is the observation of the horizontal growth of gallium oxide nanowires on substrates. With the exceptions of a few studies on the horizontal growth of ZnO, In$_2$O$_3$ and TiSi$_2$ nanowires on sapphire and silicon substrates, there are essentially no reports describing the direct horizontal growth of nanowires on a substrate surface using the vapor phase transport method [17–19]. We have identified the substrate condition favorable for the extensive growth of long horizontal Ga$_2$O$_3$ nanowires, and verified their identity by TEM characterization.

2. Experimental details

Gallium metal (Strem, 99.99%) was used as the gallium source for the growth of Ga$_2$O$_3$ nanowires and nanobelts. A drop of gallium metal (∼0.5 g) was added to one end of a quartz boat. Si(111) or Si(100) wafers cut to 12 mm × 12 mm were first boiled with piranha solution (H$_2$SO$_4$:H$_2$O$_2$ in 4:1 volume ratio) for 45 min and in water for another 45 min, followed by sonication in acetone and 2-propanol for 5 min each. The same nanowires and nanobelts can be obtained using either silicon wafer. After being dried with a nitrogen stream, these substrates were sputtered with a 3 nm gold thin film for nanowire growth, and cut into two smaller pieces. For the patterned growth of Ga$_2$O$_3$ nanowires and nanosheets, a 200 mesh copper grid was placed on a substrate as a mask to pose the top silicon oxide layer, which was transferred to a TEM grid for examination. Powder x-ray diffraction (XRD) patterns were taken with a MAC Science MXP18 diffractometer with Cu Kα radiation. Diffuse reflectance spectra of the samples were obtained on a Hitachi U-3310 spectrophotometer equipped with an integrating sphere. Photoluminescence spectra were collected on a Hitachi F-4500 fluorescence spectrophotometer with a solid sample holder.

3. Results and discussion

In this study, Ga$_2$O$_3$ nanowires and nanobelts were grown using a simple vapor transport process on silicon substrates coated with a thin gold catalyst film. Two substrates were placed in the tube furnace as shown in figure 1. Interestingly, somewhat different Ga$_2$O$_3$ nanostructures were obtained from these two substrates despite their closeness to the gallium metal source. Figure 2(a) gives an FE-SEM image of the
as-synthesized nanowire and nanobelt structures grown on substrate I. Extensive growth of nanowires and nanobelts can be seen. The nanobelts have widths of several hundred nanometers to a few microns and thicknesses of 100 nm to several hundred nanometers. These nanobelts appear very straight and stiff despite their long lengths. They may also possess some zigzag regions along the lengths of the nanobelts, and terminate with a sharp end. The overall structure of a nanobelt resembles that of a very long sword. The nanowires were found to have diameters of around 100 nm. The majority of the 1D nanostructures are nanobelts. These nanowires and nanobelts can grow to exceptionally long lengths of hundreds of microns and even over 2 mm, as illustrated in figure 2(b). To the best of our knowledge, this is the first time that the entire lengths of ultralong Ga$_2$O$_3$ nanowires and nanobelts have been presented. These nanobelts and nanowires can grow to such long lengths due to a relatively long growth time of 5 h, ample supply of the gallium vapor, and possibly their straight and rigid structure. The oxygen source may be from a trace amount of oxygen in the furnace tube, nitrogen gas cylinder, and/or a thin oxide film on the substrate. The growth mechanism of these nanobelts is believed to be gold-catalyzed, as is the case for the nanowires (see discussion below). However, their rapid upward and side growth to such large dimensions suggests that the crystal growth is spontaneous, and the gold catalyst is not important after the very initial stage. The gold catalyst probably stays on the substrate, and does not appear at the tips of these nanobelts. Upon irradiation with UV light, these Ga$_2$O$_3$ nanobelts and nanowires exhibit strong blue emission. Figure 2(c) shows an optical image of the dense growth of ultralong Ga$_2$O$_3$ nanobelts and nanowires over the entire substrate. A bright blue color was visible when the sample was irradiated with 254 nm light from a handheld UV lamp. Such highly luminescent property of the Ga$_2$O$_3$ nanostructures has been reported, but optical images of these 1D nanostructures showing their brightly blue luminescent color have not been provided before. Figure 3 is the XRD pattern of the nanobelts and nanowires grown on substrate I. The three strongest peaks are the (002), (111), and (202) peaks of Ga$_2$O$_3$ at 31.72, 35.22, and 38.42° 2θ, respectively. The diffraction pattern and peak positions match very well with those of monoclinic β-Ga$_2$O$_3$ with lattice constants $a = 12.23$ Å, $b = 3.04$ Å, $c = 5.80$ Å, and $\beta = 103.7°$ (JCPDS file 43-1012), and confirms that the nanostructures formed are indeed crystalline β-Ga$_2$O$_3$ nanobelts and nanowires.

The Ga$_2$O$_3$ nanostructures grown on substrate II vary significantly, depending on the distance of a region on the substrate from the gallium metal source. Figure 4(a) gives an SEM image of the nanowires grown at the region closest to the gallium metal (3–5 mm from the gallium metal). Mostly nanowires and some nanobelts were formed here. The nanowires generally have diameters in the order of tens of
nanometers, and can reach lengths of hundreds of microns. A distinct feature is the observation of nanowires with side growth to form sheetlike structures. This structural feature is possibly a result of an ample supply of gallium vapor to directly deposit Ga₂O₃ layers on the surfaces of pre-formed β-Ga₂O₃ nanowires through an epitaxial growth mechanism [20]. Interestingly, these sheetlike structures were only found in this small region. Figure 4(b) presents an SEM image of Ga₂O₃ nanowires grown on substrate II at a distance of 6–8 mm away from the gallium metal. Clearly only nanowires were formed in this region. The nanowires are shorter here, but can still reach lengths of tens of microns. The diameters of the nanowires are largely on the order of tens of nanometers. Their shorter lengths and the absence of the sheetlike structures suggest that much less gallium vapor has reached this zone. Upon close examination, catalyst particles can be observed at the tips of these nanowires. These nanoparticles should be the gold catalyst particles. This feature shows that these nanowires were formed by the vapor–liquid–solid (VLS) growth mechanism.

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Figure 4(d) presents an SEM image of Ga₂O₃ nanowires grown on substrate II at a distance of 6–8 mm away from the gallium metal. The absence of a continuous supply of gallium vapor for nanowire growth is clearly seen here. Many short nanowires appear to lie on the substrate, due possibly to the lack of a continuous supply of gallium vapor for nanowire growth. A nanowire lying flat on the substrate surface is shown in figure 4(d). This nanowire also contains a catalyst particle at the tip of the wire. The observation of this horizontal nanowire growth, and the possible source of oxygen coming from the thin oxide film on the substrate, suggest the possibility of enhancing the horizontal nanowire growth via increasing the oxide film thickness (to be discussed later).

A detailed structural characterization of the as-synthesized Ga₂O₃ nanowires and nanobelts was carried out. Figure 5(a) shows a TEM image of a single Ga₂O₃ nanowire grown on substrate II. This nanowire has a diameter of 27 nm, and appears to contain small ridges over the wire length. Energy-dispersive x-ray spectroscopic (EDS) analysis of the catalyst particle revealed strong signals for Au, and virtually no signals for Ga (data not shown). On the other hand, analysis of the nanowire produced strong Ga and oxygen signals, but no peaks for Au. The results confirm the formation of these nanowires through a VLS growth mechanism. The selected-area electron diffraction (SAED) pattern of this nanowire recorded along the [101] zone axis reveals the single-crystalline nature of this nanowire (figure 5(b)). The high-resolution TEM image of the rectangular region in panel (a) is provided in figure 5(c). Adjacent lattice fringes with a d-spacing of 2.30 Å were obtained, which should correspond to the (202) lattice planes. This result is consistent with the SAED pattern obtained, showing that the nanowire grows along the [101] direction.

We noticed that 1D Ga₂O₃ nanostructures have been reported to show many different growth directions, presumably because their monoclinic crystal structure does not have any strongly preferred growth direction as hexagonal ZnO nanowires do. The TEM image of a fractured Ga₂O₃ nanobelt after sonication is given in figure 6(a). This nanobelt has a width of 780 nm. Figure 6(b) presents the high-resolution TEM image of the rectangular region in panel (a) and the SAED pattern for this nanobelt recorded along the [111] zone axis. Clear lattice fringes can be discerned with a d-spacing of 2.06 Å, which should correspond to the (112) lattice planes, and is consistent with the SAED pattern recorded.

The optical properties of the ultralong Ga₂O₃ nanobelts and nanowires grown on substrate I were characterized. Figure 7(a) displays the diffuse reflectance spectrum of the Ga₂O₃ nanobelts and nanowires. To further determine the band gap of these nanostructures, a plot of (αhν)² versus hν was made, and is shown in the inset of figure 7(a). The band gap of the β-Ga₂O₃ nanobelts and nanowires was determined as 4.56 eV. A band gap value of 4.60 eV was obtained for β-Ga₂O₃ powder purchased from Alfa Aesar (99.999%). Previous studies on 1D Ga₂O₃ nanostructures have not presented the optical absorption data for comparison.
Figure 7. (a) Diffuse reflectance spectrum of the Ga$_2$O$_3$ nanowires and nanobelts grown on substrate I. The inset shows a plot of $(\alpha h\nu)^2$ versus $h\nu$ for the determination of the direct band gap of the nanowires and nanobelts. The numerical values of $(\alpha h\nu)^2$ may not be right due to a lack of information on the sample thickness or path length. (b) Photoluminescence spectrum of the Ga$_2$O$_3$ nanowires and nanobelts excited at 254 nm. There is no emission peak at 340 nm; this peak-like feature results from the use of a 290 nm filter to remove the excitation light.

Figure 7(b) is a photoluminescence spectrum of these nanobelts and nanowires excited at 254 nm. A strong blue emission band centered at 470 nm was observed. Ga$_2$O$_3$ nanowires have been reported to show a luminescence peak at 475 nm [3]. The blue emission has been proposed to originate from the recombination of an electron on a donor formed by the oxygen vacancies and a hole on an acceptor formed by the gallium vacancies [1, 21]. Because the donor band lies below the conduction band, and the acceptor level is higher than the valence band, this smaller energy transition results in the generation of blue emission [1]. The single emission band profile recorded suggests that our synthesized nanobelts and nanowires do not possess various kinds of defect, which may result in multiple emission peaks as have been observed in some studies [4a, 6, 14]. No near-band-edge emission was detected using excitation wavelengths of 200–240 nm.

To further explore the possibility of enhancing the observed horizontal growth of Ga$_2$O$_3$ nanowires on substrates, clean Si(111) or Si(100) substrates were first etched with HF solution to remove the native oxide layer, and then annealed in an oxygen atmosphere at 900 °C for 5 hr to obtain a silicon oxide film of ~100 nm in thickness. Figure 8(a) is an SEM image showing the patterned growth of Ga$_2$O$_3$ nanowires and nanobelts without this silicon oxide film. No horizontal nanowire growth was observed in the regions covered by a 200 mesh copper grid during the gold film deposition process. In contrast, some horizontal nanowires were grown over the covered regions on a substrate with this thick silicon oxide film, as shown in figure 8(b) and the supplementary data (available at stacks stacks.iop.org/Nano/19/155604). Many of these horizontally grown nanowires have diameters of several tens of nanometers to ~100 nm, and lengths of a micron or over
10 \mu m. Catalyst particles can also be observed. Direct EDS analysis of these nanowires on the silicon substrate yielded low gallium signals because of a relatively large electron beam spot and a low nanowire density. To obtain more solid evidence of the composition of these horizontal nanowires, the silicon substrate was removed to leave just the top silicon oxide film for TEM characterization. Figure 8(c) is a TEM image of a single nanowire with a diameter of 55 nm grown on the SiO$_2$ layer. EDS analysis of this nanowire gave strong signals for Ga, Si, and O (data not shown). The high-resolution TEM image of a portion of this nanowire revealed two sets of lattice fringes with $d$-spacings of 3.47 and 2.45 Å at an angle of 91°, which are consistent with the (201) and (211) lattice plane assignments of $\beta$-Ga$_2$O$_3$, as determined by the CaRIne Crystallography program (figure 8(d)).

The results confirm the identity of these horizontal nanowires as $\beta$-Ga$_2$O$_3$ nanowires. Figure 8(e) provides a TEM image of a larger area of this oxide film with some horizontally grown Ga$_2$O$_3$ nanowires. EDS analysis of the dark catalyst particle at the end of one nanowire gave strong signals for Au, suggesting the same VLS growth mechanism for these horizontal nanowires. It is assumed that these horizontal Ga$_2$O$_3$ nanowires mostly originated from the gold catalyst particles in the square-patterned regions and grew toward the mask-covered regions. The SiO$_2$ layer may also provide the oxygen source to facilitate this horizontal growth. The nanowires may change their growth directions due to strong interactions with the surface oxide layer, or upon contacting with another nanowire. Currently the attempt to control the growth direction of these horizontal nanowires via a strong carrier gas flow is not successful, because the interactions between the nanowires and the oxide film are considered much greater. Since there are practically no examples of simple and direct horizontal nanowire growth on substrates, this approach may be exploited and extended to other oxide nanowire systems.

4. Conclusion

We have successfully grown ultralong $\beta$-Ga$_2$O$_3$ nanowires and nanobelts on silicon substrates using a vapor phase transport method. Their full lengths of hundreds of microns and even millimeters have been presented for the first time. XRD patterns and TEM images have been used to characterize their crystal structures. These nanostructures give highly blue luminescence upon irradiation with a UV lamp. The blue emission has a band maximum at 470 nm. Enhanced horizontal Ga$_2$O$_3$ nanowire growth can be achieved by annealing the substrates in oxygen to form a thick SiO$_2$ film. The discovery of this unusual horizontal nanowire growth warrants further investigation, and the extension of possible horizontal nanowire growth to other oxide systems using this approach. The ability to control the direction and lengths of horizontal nanowires grown directly on substrates should be important for the fabrication of nanodevices.

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