Direct synthesis of beta gallium oxide nanowires, nanobelts, nanosheets and nanograsses by microwave plasma

Feng Zhu *, Zhong Xue Yang, Wei Min Zhou, Ya Fei Zhang

National Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Institute of Micro and Nano Science and Technology, Shanghai Jiaotong University, 1954 Huashan-Road, Shanghai 200030, People’s Republic of China

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Abstract

In this study, beta-gallium oxide (β-Ga2O3) nanowires, nanobelts, nanosheets, and nanograsses were synthesized through microwave plasma of liquid phase gallium containing H2O in Ar atmosphere using silicon as the substrate. The nanowires with diameters of about 20–30 nm were several tens of microns long and the nanobelts with thickness of about 20–30 nm were tens to hundreds of microns long. The morphology and structure of products were analyzed by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and X-ray diffraction (XRD). These results showed that multiple nucleation and growth of β-Ga2O3 nanostructures could easily occur directly out of liquid gallium exposed to appropriate H2O and Ar in the gas phase. The growth process of β-Ga2O3 nanostructures may be dominated by VS (vapor–solid) mechanism.

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1. Introduction

Nanometer-scale structures are known to have great prospects in fundamental physical science and novel nanotechnological applications, because of their importance in understanding the basic concepts of the roles of both dimensionality and quantum size effects [1–3]. Functionalization of these nanostructures can only be achieved and become useful through the synthesis of bulk quantities of defined structures with controlled morphology. As a wide-band gap ($E_g = 4.9$ eV) semiconductor, monoclinic gallium oxide (β-Ga2O3) possesses conduction and luminescence properties and thus has potential applications in optoelectronic devices including flat-panel displays, solar energy conversion devices, optical limiter for ultraviolet, and high temperature stable gas sensors [4–9]. Nanostructures of gallium oxide will be of particular interest for these applications.

Recently, β-Ga2O3 nanostructures have been synthesized by various high-temperature methods, including the thermal evaporation method, arc-discharge method, carbothermal reduction, laser ablation method, and so on [10–13]. However, there are rare studies on the synthesis of gallium oxide nanostructures using microwave plasma, which rapid evaporation and decomposition of precursor materials results in nanostructures of high purity. In addition, microwave plasma demonstrates good stability, uniform temperature field and at normal ambient pressure, which can be controlled in a range of 300–900 °C [14].

In this paper, we introduce bulk nucleation and growth of β-Ga2O3 nanostructures directly through microwave plasma. The synthetic reaction was carried out in microwave plasma chamber at 600 W with a Ga droplet as the source, H2O as the monomer and Ar as the carrier gas, which we believe, has nerve been reported. It was found that β-Ca2O3 nanowires, nanobelts, nanosheets, and nanograsses could easily be formed simply through the reaction liquid Ga with H2O. In addition, we present the synthesis of unique geometrical structures of β-Ga2O3 in the form of nanograsses. The nanowires with diameters of about 20–30 nm were up to tens of microns long and the nanobelts with thickness of about 20–30 nm were tens to hundreds of microns long. Furthermore, this method does not need any catalyst, so avoiding catalyst contamination.
2. Experiment

Synthesis was carried out in a microwave plasma reactor (MPG 2010P 1 KW) with H$_2$O. The schematic diagram of arrangement of the substrate and the liquid Ga metal with respect to the plasma ball is described in Fig. 1.

Analytical grade Ga droplet (0.3 g, purity greater than 99.99%) and the silicon substrate were placed on the holder (40 mm in diameter) and positioned horizontally in the chamber of microwave plasma reactor. The Ga droplet placed on the silicon substrate was exposed to a microwave plasma. During the plasma exposure, the gallium droplets formed intentionally nuclei which be put on substrates and further synthesis experiments were carried out. The nanostructures discussed in this paper were grown from these gallium drops. The substrate temperature was measured by an infrared pyrometer to be approximately 550°C for 600 W microwave power, 40 Torr total pressure, and 100 sccm (standard cubic centimeters per minute) of H$_2$O in 100 sccm of carrier gas of high-purity Ar in the inlet stream. The experiments were performed at the following range of growth conditions: microwave power of 600–900 W, pressure of 30–60 Torr, growth duration of 1–6 h, 100 sccm of H$_2$O and 100 sccm of Ar.

The collected products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM at 300 kV) and energy-dispersive X-ray spectroscopy (EDX). For SEM investigations, the products together with the silicon substrates were directly transferred into the SEM chamber, without destroying the location and orientation of the products on the substrate. For TEM studies, some samples were scraped off from the silicon substrates and were directly mounted on Cu.

3. Results and discussion

The resulting products, which appeared like a piece of white wool-like materials, were collected on the surface of silicon substrates around the residual Ga droplet, covering an approximately 10 mm region.

The overall structure of the synthesized products was characterized by XRD. Fig. 2 displays the XRD patterns taken from the products on silicon substrates. Miller indices are indicated on each diffraction peak. It can be seen that the whole spectrum can be indexed from peak positions to a monoclinic crystalline Ga$_2$O$_3$ phase, which is in good agreement with the reported values of β-Ga$_2$O$_3$ with the lattice constants $a = 12.23$ Å, $b = 3.04$ Å, $c = 5.8$ Å and $β = 103.7^\circ$ (JCPDS: 43-1012). No crystalline phases other than silicon were found within the detection limit. The silicon diffraction peaks come from the substrate. Hence, the as-synthesized products are pure, well-crystallized β-Ga$_2$O$_3$. It is noted that the relative intensity of the peaks is not consistent with that of bulk Ga$_2$O$_3$ (the most intensive peak is (111) for the bulk, instead of the (202) as in the present case), which may frequently happen for nano-size structures, and is understandable because of the size-effect and disorder arising from nanostructures.

Fig. 3, showing SEM image of as-prepared materials, reveals that these products consist of nanowires (several to several tens of microns long and 20–30 nm of diameter), nanobelts (several tens to several hundreds of microns long and 20–30 nm of thickness), nanosheets and nanograsses. Fig. 3(a) shows the low-magnification of nanowires, which can be obtained on top of micron-sized to millimeter-sized residual Ga near center of substrate. It is also noted that the products consists of a large quantity of quasi-one-dimensional thin structures, nanobelts and nanosheets, around the micron-sized to millimeter-sized residual Ga in Fig. 3(b). The high-magnification SEM images of nanowires, nanobelt and nanosheet are given in Fig. 3(c)–(e), respectively. In addition to the above nanostructures, we obtained nanostructures with grasses morphology on the edges substrate stage around the substrate, which was toward the edge of the dense plasma region (Fig. 3(f)). The in situ EDX analysis showed only the elements Ga and O were present (results not shown), indicating the formation of gallium oxide. Which is consistent with the XRD results. From the results of SEM, it can be found the size of the products increase with the distance from the residual Ga droplet. Table 1 shows that different kinds of nanostructures were collected from different zone of the substrate. In our current plasma reactor setup, a ball-shaped plasma sits at the
center of a substrate stage, which makes conditions (radial densities) different radial positions.

The structure and morphology of the β-Ga2O3 nanowire and nanobelt were further characterized using TEM. The low-magnification TEM images of a straight individual β-Ga2O3 nanowire and nanobelt are displayed in Fig. 4(a) and (c). It can be found that nanowire has a uniform diameter and nanobelt has a uniform width and flat surface, which is accordant with SEM results. High-resolution TEM (HRTEM) images shown in Fig. 4(b) and (d) of the nanowire and nanobelt reveal that a clean and structurally perfect surface. The clear lattice fringes in the HRTEM images indicate a single crystal structure of the nanowire and nanobelt. The insets show the Fourier diffractogram obtained from the HRTEM image of Fig. 4(b) and (d), indicating a crystalline nature and the direction of nanowire and nanobelt axis to be \([-1\,0\,1]\), \([1\,0\,1]\). So in the image Fig. 4(b) and (d), the direction \([-1\,0\,1]\) and \([1\,0\,1]\) are the growth direction of the nanowire and nanobelt, respectively, which are indicated by arrows. The spacing of about 0.28 and 0.23 nm between arrowheads correspond to the distance between \((-\,2\,0\,2),\,(2\,0\,2)\) planes. The surfaces of the nanowire and nanobelt are clean, atomically sharp, and unsheathed amorphous phase.

VLS (vapor–liquid–solid) and VS (vapor–solid) are two dominant mechanisms in the growth of low-dimensional

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Location on substrate</th>
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<tbody>
<tr>
<td>Nanowires</td>
<td>On top of micron-sized to millimeter-sized residual Ga near the center of substrate</td>
</tr>
<tr>
<td>Nanobelts</td>
<td>Around micron-sized to millimeter-sized residual Ga</td>
</tr>
<tr>
<td>Nanosheets</td>
<td>Around micron-sized to millimeter-sized residual Ga</td>
</tr>
<tr>
<td>Nanograsses</td>
<td>Near edges of substrate</td>
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Fig. 4. TEM and HRTEM image of as-prepared β-Ga₂O₃ nanowire and nanobelt: (a) low-magnification TEM image of individual nanowire; (b) HRTEM image of the nanowire, showing a clean and structurally perfect surface, the inset is the Fourier diffractogram obtained from the HRTEM image; (c) low-magnification TEM image of individual nanobelt; (d) HRTEM image of the nanobelt, showing a clean and structurally perfect surface, the inset is the Fourier diffractogram obtained from the HRTEM image.

Fig. 5. Schematic depicting possible growth routes for multiple nanowires, nanobelts, nanosheets, and nanograsses of β-Ga₂O₃.
nanostructures. As no catalyst was involved and liquid H₂O changed into vapor H₂O at 600 W, the underlying growth of β-Ga₂O₃ nanostructures was by VS process in our experiment. The key of VS mechanism is nucleation and growth of oxide nanostructures. We assume that the nucleation and growth of oxide nanostructures occurs in two basic steps: (a) reaction between H₂O and Ga to form oxygenated gallium species into gallium droplets and create different kinds of nuclei on the substrate, (b) growth of nuclei into nanostructures from the bottom by use of the species and supersaturation. In the present work, β-Ga₂O₃ species were formed on silicon substrate by a simple chemical reaction as follows:

\[ 2Ga + 3H₂O \rightarrow Ga₂O₃ + 3H₂ \]

and a ball-shaped plasma makes different conditions at different radical positions on the silicon substrate, so the reaction of step (a) can be implement to form oxygenated gallium species to create different kinds of nuclei on the different silicon substrate zone. It is now generally accepted that the control of supersaturation is a prime consideration in obtaining nanostructures from the vapor phase, because there is strong evidence that the degree of supersaturation determines the prevailing grow morphology [15]. A low supersaturation is required for low-dimensional nanostructures growth. Ga has a wide temperature range in the liquid phase (from 29.78 to 2403 °C) and low vapor pressure, which can guarantee a suitable supersaturation for the β-Ga₂O₃ nanostructures to nucleate and grow from the vapor phase. The step (b) is also easy to fulfill. The schematic diagram of different nanostructures grown by microwave plasma is described in Fig. 5.

4. Conclusion

Different nanostructures of β-Ga₂O₃, such as nanowires, nanobelts, nanosheets and nanograsses, were directly synthesized through microwave plasma using liquid gallium metal and H₂O as the raw materials. It is to form these different nanostructures because plasma makes different radical conditions on the silicon substrate. The growth of β-Ga₂O₃ nanostructures was explained by the VS synthesis mechanism. These β-Ga₂O₃ nanostructures are expected to possess interesting properties for nano-technological application in the future.

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References