β-Ga_2O_3 nanorods crossing perpendicularly each other on MgO (100) substrate

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Growth and characterization of nanowires and nanorods of wide bandgap (E_g) compounds [1–14] have attracted much attention due to significant potential of such one-dimensional materials for optoelectronic applications [15, 16] It was reported that transparent β-Ga_2O_3 ($E_g \approx 4.9$ eV) [17] has potential application in optoelectronics [18], and nanometer-scale Ga_2O_3 exhibits particular optical and electrical properties [19]. β-Ga_2O_3 is intrinsically an insulator useful for all gallium-based semiconductors but becomes an n-type semiconductor when synthesized under reducing conditions. Recent requirements for improved transparency and higher conductivity have led to explore new transparent conducting oxides available in a variety of devices including low-power driven flat-panel displays and high-efficiency solar energy-conversion devices. One-dimensionally structured β-Ga_2O_3 is expected to provide attractive characteristics for its practical applications as well as for fabricating nanodevices with novel properties.

Growth of the nanorods by vapor phase transport method was carried out in a horizontal furnace. A β-Ga_2O_3 single crystal[20] was pulverized and loaded in an alumina boat. The boat and the MgO substrate coated with a thin Au layer were transferred to the places of 1200 and 640 °C in an alumina tube of the furnace, respectively. In a typical run, the Au layer was evaporated in a vacuum (2×10^{-5} Torr) on the substrate, and the layer consisted of Au nanospheres with about several tens of nanometers in diameter. First, the tube was pumped out by a rotary pump, and then it was heated up to 1200 °C at the rate of 10 °C/min in a flow of mixed gas (95% N_2 and 5% H_2). The substrate placed downstream of the gas flow. At 1200 °C, the temperature was kept constant for 180 min. After cooling down to room temperature, a white layer was found on the substrate. The white layer was characterized by using a JEOL JSM-6320F scanning electron microscope (SEM), a JEOL JEM-3100FEF transmission electron microscope (TEM) operated at 300 kV, an energy dispersive X-ray spectrometer (EDX) equipped to the microscope, and a Rigaku CN2031 X-ray diffractometer (XD) with Cu Kα radiation. Optical emission spectrum in ultraviolet-visible region was measured under 240 nm-line irradiation using a JASCO V-560 spectrometer.

As shown in Fig. 1a, a low magnification SEM image revealed that the white layer consists of a large quantity of conical shaped nanorods crossing perpendicularly each other on the substrate. Most of the nanorods were straight, and typical lengths were in the range of several to ten micrometers. In a high magnification image of Fig. 1b, we see that the diameter was up to one micrometer around the root of the conical nanorods but decreased to few hundreds nanometers on approaching the tip. Such typical values in the length and diameter result in a very large aspect ratio for the nanorods, which are in the range of approximately 10–50. As seen in Fig. 1b, each nanorods had a nanosphere with diameters of few hundreds nanometers at the tip. The diameter

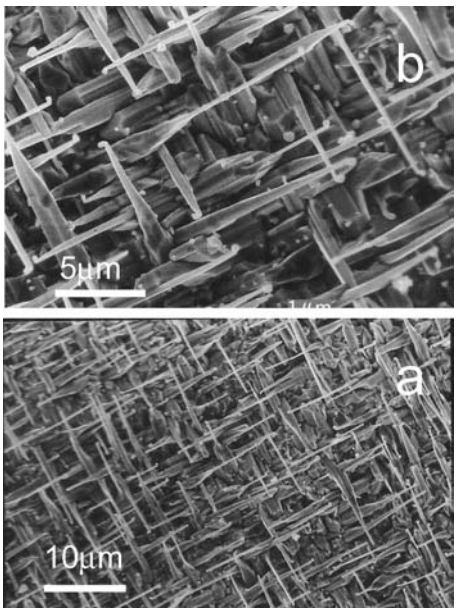

Figure 1 SEM images with relatively low (a) and high (b) magnification of β-Ga_2O_3 nanorods grown on MgO (100) substrate.

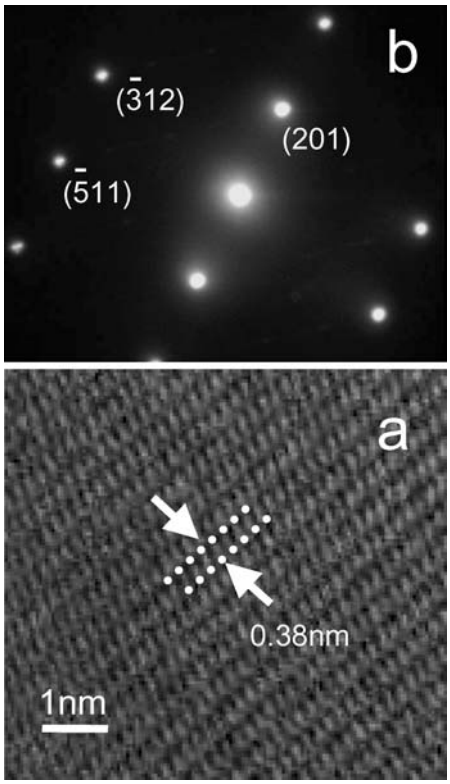

Figure 2 Lattice image (a) and electron diffraction pattern (b) of a β-Ga_2O_3 nanorod by TEM.

of the nanosphere looks larger than that of the nanorod nearby the tip.

The crystal structure of the nanorods was characterized by TEM and XD. Elemental analysis of individual nanorod was performed using EDX equipped to the TEM. For TEM observation, the nanorods were scraped away from the substrate surface and dispersed in ethanol, and then the ethanol solution was sprayed onto a copper grid coated carbon film. A structure image of a nanorod with clear lattice fringes of β-Ga_2O_3 was obtained, as shown in Fig. 2a. The periodicity of 0.38 nm between the arrowheads corresponds to distance between the (201) planes of β-Ga_2O_3 crystal. No microtwins, stacking faults, and other planer defects were found in some nanorods. An electron diffraction pattern of the nanorod shown in Fig. 2b can be indexed to the monoclinic β-Ga_2O_3 (JCPDS 11-370). Some Miller indices were labeled on the spots. All spots can be attributed to the structure with lattice constants of $a = 1.223$ nm, $b = 0.304$ nm, $c = 0.580$ nm, and $\beta = 103.7^\circ$, and with the space group of C2/m. The nanorods gave an XD pattern mirroring epitaxial growth of β-Ga_2O_3 crystal on the substrate, as shown in Fig. 3. The (400) plane of the β-Ga_2O_3 nanorods is parallel to the (100) plane of the MgO substrate. The EDX analysis indicated that the nanorods are composed of Ga and O. The Ga/O ratio of the nanorods was consistent with that of single crystalline β-Ga_2O_3 [21]. Emission spectrum was measured to examine the optical property of the β-Ga_2O_3 nanorods. While the β-Ga_2O_3 crystalline powders used as raw material in this experiment exhibited blue-emission centered at 400 nm under illumination of 240 nm-light, the β-Ga_2O_3 nanorods showed no emission due to the defects such

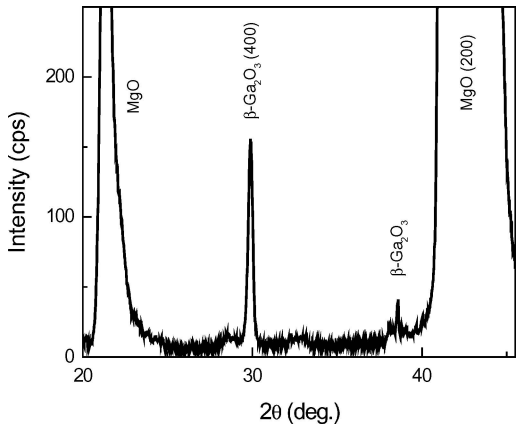

Figure 3 XD pattern of the β-Ga_2O_3 nanorods grown on MgO (100) substrate. The peak at $2\theta \approx 30^\circ$ can be assigned to reflection from the (400) plane of β-Ga_2O_3. At $2\theta \approx 39^\circ$, we see a weak signal ascribable to reflection from the (311) plane of β-Ga_2O_3. Peaks at $2\theta \approx 21^\circ$ and $\approx 42^\circ$ are due to the MgO substrate. Most of the nanorods grew eptaxially on the substrate. The β-Ga_2O_3 (400) plane was parallel to the MgO (100) plane.

as oxygen vacancies and Ga-O vacancy pairs under such illumination. The optical emission spectrum confirmed a high-quality crystal growth of the nanorods. These are in good agreement with the result of structural characterization.

There are two models for the growth of conventional crystal nanorods, the screw dislocation and vapor-liquid-solid (VLS) process. As shown in Fig. 1b, each elongated nanorods terminates in a nanosphere at the tip. EDX analysis indicated that the nanosphere on the tip consisted of Au but the stem was constructed with Ga_2O_3. The Au nanosphere looks larger than the β-Ga_2O_3 nanorod nearby the tip. In our TEM observation, the surfaces of the β-Ga_2O_3 nanorods were clean and there was no sheathe of amorphous phase. These results suggest that the growth of the nanorods may be dominated by the VLS process [22]. In VLS growth process, a metal particle is located at the growth front of the rod and acts as the catalytic active site. The solidified spherical droplets at the tips of the nanorods are commonly considered to be the evidence for the operation of the VLS mechanism, which is in agreement with our results.

Here, we have reported growth of β-Ga_2O_3 nanorods capped with Au nanosphere. The conical nanorods consisting of monoclinic β-Ga_2O_3 single crystals crossed perpendicularly each other on the (100) plane of the MgO substrate. Typical lengths of the nanorods were in the range of several to ten micrometers. Diameters were up to one micrometer around the root of the conical nanorods and decreased to few hundreds nanometers with approaching to the tip. The Au nanospheres with diameters of few hundreds nanometers placed at the tip. The Au nanosphere played a crucial role in the growth of β-Ga_2O_3 nanorods based on the VLS mechanism.

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