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Synthesis of β-Ga_2O_3 nanowires by an MOCVD approach

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ABSTRACT We have synthesized monoclinic gallium oxide (β-Ga_2O_3) nanowires on Au-coated Si substrates by a reaction of a trimethylgallium and oxygen mixture. The β-Ga_2O_3 nanowires became progressively thinner from bottom to top, with diameters ranging from 10 to 200 nm and lengths of several micrometers. We found that Au-containing nanoparticles were attached to the tips of the β-Ga_2O_3 nanowires and thus the nanowire growth could be a vapor–liquid–solid process.

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1 Introduction

One-dimensional (1-D) nanostructures are of great interest for their novel physical properties [1–4]. Recently, much attention has been paid to nanowires [5–10] of the family of oxides, and several binary oxide nanowires such as MgO [5], SiO_x [6], In_2O_3 [7], GeO_2 [8], ZnO [9], and AlO_x [10] have been synthesized.

Since β-Ga_2O_3 with a wide band gap ($E_g = 4.9$ eV) [11] has great potential application in optoelectronic nanodevices and gas sensors, many researchers have worked on the growth of Ga_2O_3 nanowires by various techniques such as physical evaporation of Ga powders [12], arc discharge of GaN powders with a transition-metal catalyst [13], thermal annealing of milled GaN powders [14], heating of GaAs and Au [15], and using a reaction with a mixture of Ga_2O_3 powder and graphite [16] or a mixture of Ga_2O_3 powder and carbon nanotubes [17]. However, to the authors' knowledge, synthesis of β-Ga_2O_3 nanowires using the metal organic chemical vapor deposition (MOCVD) method has not been reported to date. In this paper, we describe the generation of β-Ga_2O_3 nanowires on Si substrates with an Au catalyst. We have used a simple reaction of a trimethylgallium (TMGa) and O_2 mixture.

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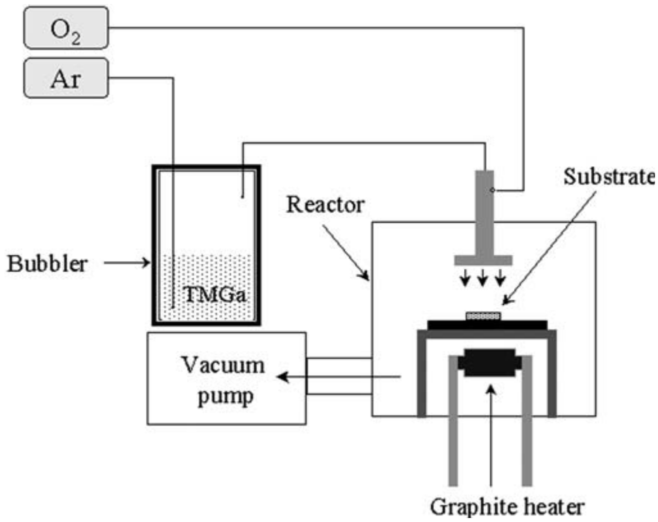

FIGURE 1 Schematic illustration of the MOCVD reactor

2 Experimental

A schematic illustration of the MOCVD reactor used in our experiments is shown in Fig. 1. We used *p*-type Si(100), precleaned with acetone and methanol, as starting material onto which a layer of Au (about 100–120 nm) was deposited by radio-frequency magnetron sputtering. The Si substrate was subsequently cut into small pieces with dimensions of 20 mm × 10 mm. In the growth process, TMGa and O_2 were used as the Ga and O sources with Ar as the carrier gas. Since TMGa and O_2 react immediately when in contact, they were introduced into the reactor separately and mixed just inside the chamber. The temperature of the TMGa bubbler was fixed at −5 °C. The Ar and O_2 gas-flow rates were set to 30 standard cubic centimeters per minute (sccm) and 6 sccm, respectively. The reactor pressure of 2 Torr was maintained during the growth for 5 min. The substrate temperature was measured to be about 700 °C. After cooling to room temperature, a thin layer of wool-like material was found on the surface of the substrate.

The resulting material was characterized by grazing incidence angle (0.3°) X-ray diffraction (XRD, Philips X'pert MRD) using Cu K_α radiation ($\lambda = 0.154056$ nm), scanning electron microscopy (SEM, Hitachi S-4200), and transmission electron microscopy (TEM, Philips CM-200) with energy-dispersive X-ray spectroscopy (EDS) installed. TEM specimens were prepared by sonicating in alcohol by ultrasonic treatment, and subsequently dropping onto a porous-carbon film supported on a copper grid.

3 Results and discussion

The whole substrate surface (200 mm^2) is found to be covered with a uniform film of dense nanowires. Statistical analysis of many SEM images shows that the deposits have diameters ranging from 10 to 200 nm and the lengths reach up to several micrometers. Figure 2a shows the typical plan-view SEM images of the deposits, indicating that this raw material consists of aggregates of 1-D nanostructures. Figure 2b shows a SEM image of the side view of the nanowires, indicating that the growth direction of the nanowires is randomized. The diameter of each nanowire gradually decreases from the bottom to the top, terminating at a nanoparticle at the tip, due to unknown changes during the deposition process. Close examination of the image reveals that the cross section of the stem of the nanowires has circular shape (not clearly shown here). Figure 2c displays a typical XRD spectrum of the nanowires. The reflection peaks of (0 0 4), ($\bar{2}$ 1 1), ($\bar{3}$ 0 4), (0 1 7), (0 2 4), ($\bar{1}$ 0 10), and (0 1 9) correspond to the monoclinic β-Ga_2O_3 structure with lattice constants $a = 5.80$ Å, $b = 3.04$ Å, and $c = 12.23$ Å (JCPDS: 11-0370), revealing the production of β-Ga_2O_3 deposits.

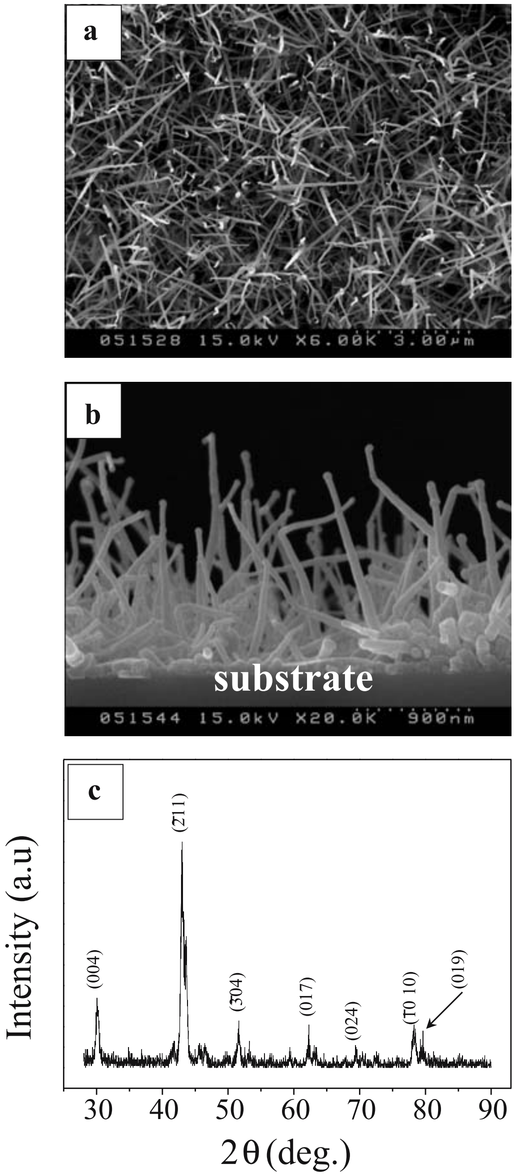

FIGURE 2 **a** Plan-view and **b** side-view SEM images of the deposited nanowires. **c** X-ray diffraction patterns recorded from the β-Ga_2O_3 nanowires

Figure 3a shows a representative TEM image of a single straight nanowire, indicating that the nanowire is in the form of a solid rod. The diameter of the nanowire becomes smaller and smaller along the growth direction to the tip, agreeing with SEM images (Fig. 2b). The nanowire has a relatively smooth surface with a minimum diameter of about 15 nm. Figure 3b reveals the visible lattice fringes of the high-resolution TEM (HRTEM) image, indicating that the nanowire is crystalline. The nanoparticle at the tip of the nanowire appears dark and has a high contrast compared with the nanowire. A thin amorphous layer of 2–3-nm thickness exists on the surface of the nanoparticle at the tip. Statistical observation of many TEM images indicates that the length direction of the nanowires is along the $\langle\bar{1}02\rangle$ direction, as shown in Fig. 3b. The magnified image in the inset shows that the spacing between parallel fringes in the length direction is 0.46 nm, corresponding to the interplanar distance of ($\bar{1}$ 0 2) lattice planes of monoclinic β-Ga_2O_3. The associated diffraction pattern in the inset exhibits a distinct ($\bar{1}$ 0 2) reflection.

EDS measurements made on the wire tip and the wire stem indicate that the nanowire tip consists of Au, Ga, and O, but the nanowire stem is composed only of Ga and O (Cu signals are generated from the microgrid mesh supporting the nanowires) (Fig. 3c). Although we do not know the exact chemical composition of the nanoparticle, we reveal that the nanoparticle comprises an Au element.

The vapor–liquid–solid (VLS) mechanism [18, 19] has been considered to be suitable for the growth of 1-D materials. In the VLS process, the nanosized liquid catalyst drops are known to serve as reactive sites, confining and directing the growth of nanowires. For the catalytic growth of β-Ga_2O_3 nanowires, the VLS mechanism, in which the tip nanoparticles serve as reactive sites, has also been suggested [15].

In the present work, in view of the presence of traces of Au in the tip nanoparticles, we surmise that the Au originates from the predeposited Au layer. The existence of nanoparticles attached to the nanowire tips implies that a VLS mechanism can be responsible for nanowire growth in this synthesis route. More investigation is underway to derive the detailed mechanism for the formation of the β-Ga_2O_3 nanowires.

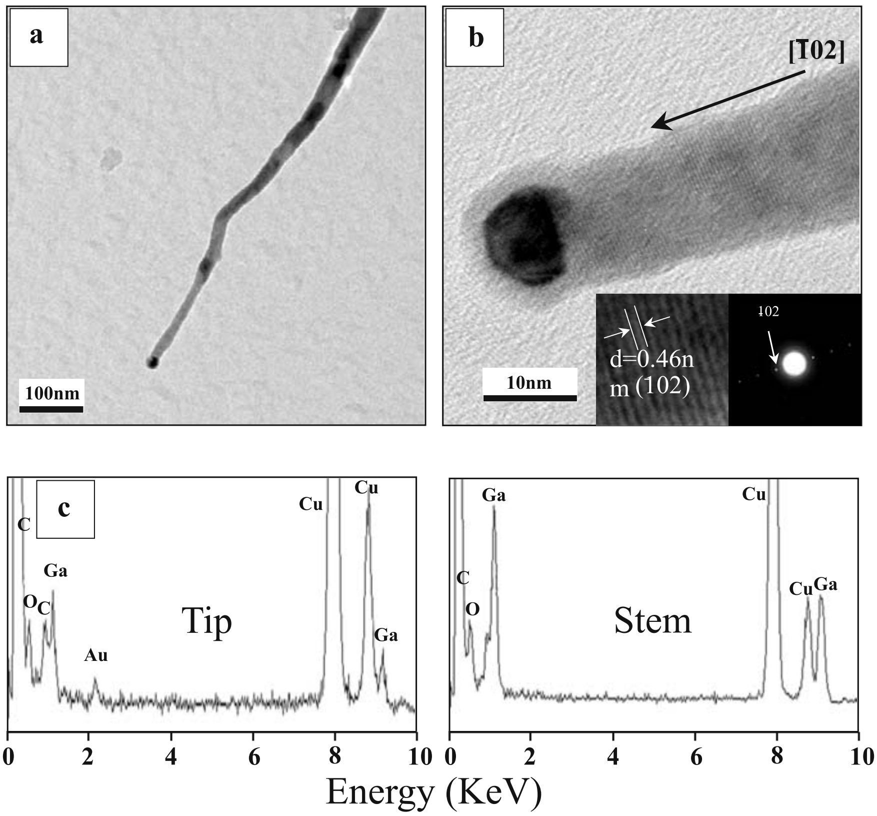

FIGURE 3 **a** TEM and **b** HRTEM images of a single β-Ga_2O_3 nanowire. The nanowire terminates with a nanoparticle. The magnified image and the corresponding electron-diffraction pattern are added in the *inset*. **c** EDS spectra of the wire tip and the wire stem

4 Conclusions

In summary, we have generated high-density β-Ga_2O_3 nanowires on Au-coated Si substrates by the MOCVD technique. XRD indicates that the obtained nanowires are monoclinic β-Ga_2O_3. The SEM image shows that the nanowires have diameters of 10–200 nm and lengths up to several micrometers. SEM, TEM, and EDS reveal that the diameter of the as-synthesized β-Ga_2O_3 nanowires decreases from the bottom to the tip, to which the Au-containing nanoparticle is attached.

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