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Catalyst-free Growth of Large Scale Ga₂O₃ Nanowires

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ABSTRACT

Large scale of straight Ga₂O₃ nanowires is grown on a fused silica substrate by a simple catalyst-free CVD method using Ga metal and N₂/H₂O reactants. The Ga₂O₃ nanowires with diameters ranging from 60 to 150 nm can be as long as several micrometers. XRD and TEM analyses indicate that the Ga₂O₃ nanowires exhibit a monoclinic structure. PL characteristic of the Ga₂O₃ nanowires shows a UV emission of 375 nm at room temperature.

INTRODUCTION

The synthesis of nanometer scale one-dimensional materials, for example β -SiC [1-3], GaN [4,5], In₂O₃ [6], and Si [7,8], has received intensive research because of their great potential for fundamental studies of the roles of dimensionality and size in their physical properties as well as for the application to optoelectronic nanodevices [9].

Gallium oxide, β -Ga₂O₃, is a wide band gap compound ($E_g = 4.9$ eV), and has potential applications in optoelectronic devices including flat panel displays, solar energy conversion devices, and high temperature stable gas sensors [10,11]. Even more, upon optical excitation through the band gap, β -Ga₂O₃ exhibit up to three different emissions, UV, blue, and green [12-14]. Recently, β -Ga₂O₃ nanowires have been synthesized by an arc discharge method [15], and physical deposition [16]. Here, we present a simple catalyst-free CVD approach for the growth of the straight β -Ga₂O₃ nanowires at a temperature of 800°C.

EXPERIMENTAL DETAILS

The schematic representation of the β -Ga₂O₃ nanowires growth apparatus is shown in Fig. 1. Typically, an excess amount of molten gallium (Alfa Aesar, 99.99%) was placed on the fused silica substrate A (1x1cm²) that was put in the end of the Al₂O₃ boat. The fused silica substrate B (1x1cm²) was put away from substrate A about 3mm. An Al₂O₃ plate (4x4cm²) put on the

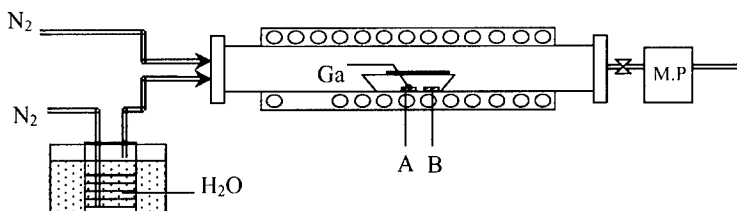


Fig. 1 Schematic diagram of the high temperature furnace used for the synthesis of the straight β -Ga₂O₃ nanowires.

top of the Al₂O₃ boat was used to increase the reactants space time in the Al₂O₃ boat. Then the Al₂O₃ boat was inserted into the center of a 3 in. diameter furnace. Before the synthesis process, the furnace was evacuated to a base pressure of 1×10^{-2} Torr. The temperature of the furnace was increased to 800°C within 1 hr at a constant N₂ flow of 200 sccm and a pressure of 500 Torr. As the temperature reached 800°C, the H₂O vapor was carried from an isothermal bath by another N₂ flow into the furnace. The synthesis processes were conducted under the following condition: furnace temperature, H₂O vapor rate, N₂ flow rate, furnace pressure of 800°C, 3 sccm, 200 sccm and 500 Torr, respectively. After the 6-hr reaction, the furnace was cooled to room temperature and white products were deposited on the fused silica substrate B.

The morphology and size distribution of the products were examined using SEM (Hitachi, S-4200). The crystal structure of the products was analyzed using XRD (Rigaku) and HRTEM (JEOL 2010), which equipped with an EDS. Micro-Raman with 514.5 nm photons was also employed to characterize the products. Photoluminescence studies were conducted with a Hitachi F-4500 fluorescence spectrophotometer with a Xe lamp at room temperature. The excitation wavelengths were 320 nm.

RESULTS AND DISCUSSION

Figure 2(a) shows a typical SEM image of the products on the fused silica substrate. Large scale of needle-like nanowires was formed with random direction on the fused silica substrate with diameters in the range of 60-150 nm. Fig. 2(b) shows a cross-sectional image of the nanowires, it reveals that the length of the nanowires is about several ten micrometers.

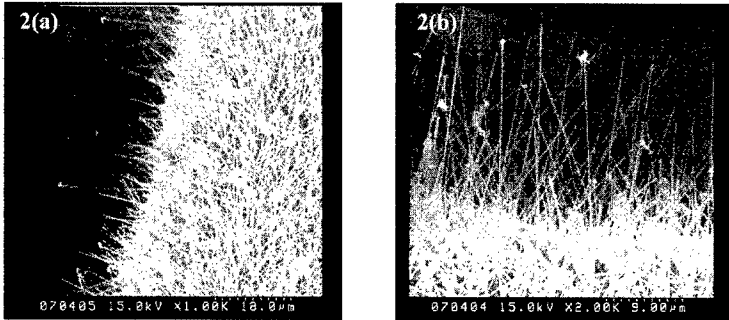


Fig.2 SEM images of large quantity of β -Ga₂O₃ nanowires grown on fused silica substrates. (a) 45° tilted view, (b) cross-section.

The typical XRD pattern of the nanowires is shown in Fig.3. The diffraction peaks can be indexed to a monoclinic structure of β -Ga₂O₃ with lattice constant $a=5.8 \text{ \AA}$, $b=3.8 \text{ \AA}$, $c=2.23 \text{ \AA}$, $\beta = 103^\circ$. Further structural characterization of the β -Ga₂O₃ nanowires was performed using TEM. As shown in Fig.4 (a), the image reveals that the surfaces of the nanowire are smooth without any step edge and sheathed amorphous phase. Moreover, there is no additional metal particle appeared at the ends of the wires, implying a non-VLS approach for the growth of the straight β -Ga₂O₃ nanowires is achieved. Fig. 4(b) shows a high-resolution TEM image of the individual nanowire. The insert shows a corresponding selected area electron diffraction pattern.

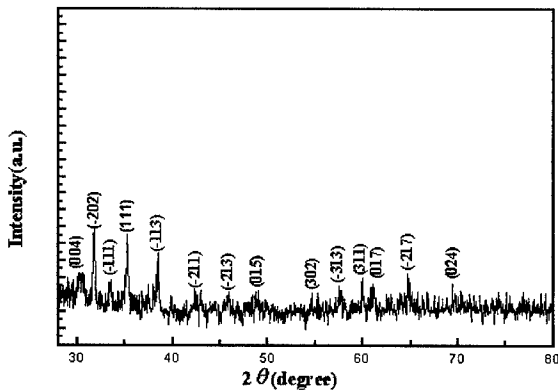


Fig.3 XRD spectrum of the synthesized product.

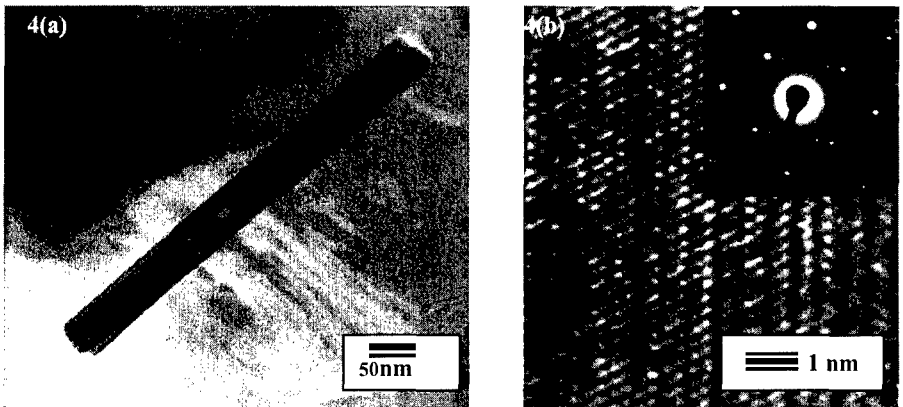


Fig.4 (a) High resolution TEM image of individual nanowire. (b) Lattice image of the individual nanowire, and a corresponding selected area electron diffraction pattern (inset).

The composition of the Gallium oxide nanowires is confirmed by EDX. As shown in Fig. 5, the EDX spectrum reveals that the nanowires are composed of gallium and oxygen without any additional metal. Quantitative analysis shows that the atomic ratio of Ga :O is about 2:3. The Raman spectrum of the β -Ga₂O₃ nanowires is shown in Fig. 6. The peaks appeared in this spectrum are consistent very well with the FT-Raman spectrum of the β -Ga₂O₃ nanowires produced by arc discharge [15].

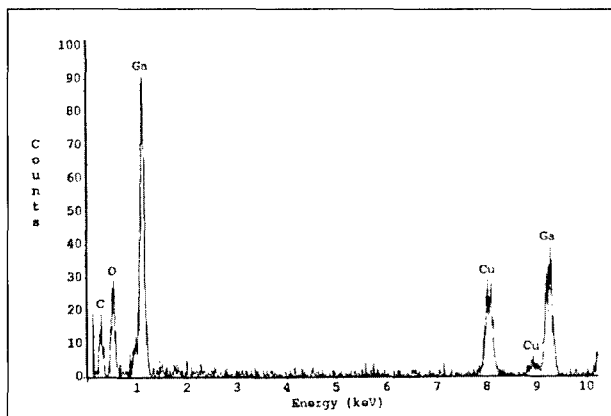


Fig.5 EDX spectrum of the β -Ga₂O₃ nanowires on a fused silica substrate.

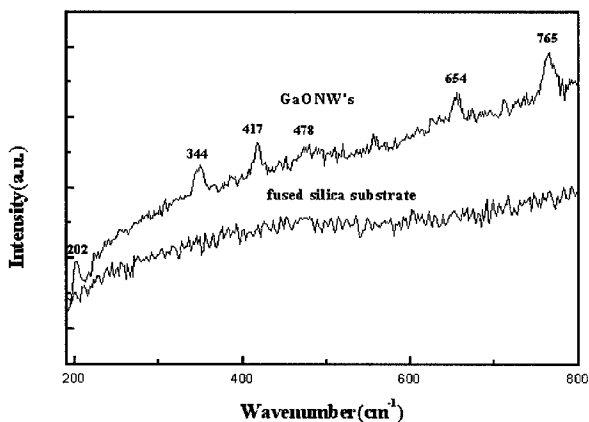


Fig.6 Raman spectrum of the β -Ga₂O₃ nanowires.

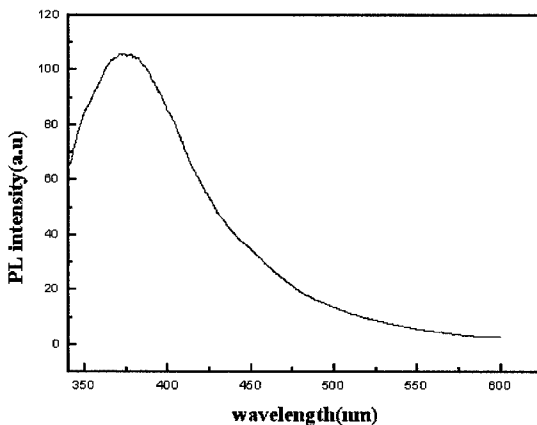


Fig.7 Typical photoluminescence spectrum of the β -Ga₂O₃ nanowires.

To examine the optical properties of the β -Ga₂O₃ nanowires, the photoluminescence(PL) measurement was conducted at room temperature. As shown in Fig. 7, the broad PL emission band is mainly located in the UV region with its maximum intensity centered at 375 nm.

CONCLUSION

Large scale of straight Ga₂O₃ nanowires was synthesized on a fused silica substrate by a simple catalyst-free CVD method using Ga metal and N₂ / H₂O reactants. The Ga₂O₃ nanowires, which have diameters ranging from 60 to 150 nm and lengths of several micrometers, are

identified to be monoclinic Ga₂O₃ using XRD. PL emission band centered at 375 nm are observed at room temperature.

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