Journal of Alloys and Compounds 489 (2010) 663–666

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Facile route to straight $ZnGa_2O_4$ nanowires and their cathodoluminescence properties

M. Lei[a], Q.R. Hu[a], X. Wang[b], S.L. Wang[a], W.H. Tang[a,*]

[a] Department of Physics, Center for Optoelectronics Materials and Devices, Zhejiang Sci-Tech University, Xiasha College Park, Hangzhou 310018, China
[b] Department of Electronic Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 20 July 2009
Received in revised form
23 September 2009
Accepted 23 September 2009
Available online 2 October 2009

Keywords:
Nanostructured materials
Semiconductors
Gas–solid reactions
Optical property

ABSTRACT

Single-crystalline $ZnGa_2O_4$ nanowires with high purity were grown on the Au and amorphous carbon layers coated Si substrates by a facile carbothermal reduction process. These $ZnGa_2O_4$ nanowires were straight along their growth direction, and the length and diameter were around 10 μm and 150 nm, respectively. The growth mechanism follows an enhanced vapor–liquid–solid (VLS) process. The carbon layers predeposited on the substrates can strongly enhance the VLS growth process of $ZnGa_2O_4$ nanowires. The cathodoluminescence (CL) spectrum of an individual nanowire exhibits a broad emission band centered at 537 nm, which can be ascribed to a large quantity of ionized oxygen vacancies.

1. Introduction

The quasi-one-dimensional (1D) systems such as nanowires and nanotubes have stimulated their functional applications and are emerging as building blocks for next generation of electronic and optoelectronic nanodevices [1–4]. As an important semiconductor with wide band gap of 4.4–4.7 eV, zinc gallate ($ZnGa_2O_4$) has attracted considerable attentions and is maybe a good candidate for light emitting diodes, photodectors, photocatalysts, low-voltage and multicolor emitting phosphors [5–9]. Up to now, the syntheses and their physical properties of $ZnGa_2O_4$ nanowires have attracted more attentions and been successfully performed. Well-known vapor–liquid–solid (VLS) and vapor–solid (VS) processes have been successfully applied in the synthesis of the $ZnGa_2O_4$ nanowires [10–14]. Moreover, direct transformation of nanowires templates to $ZnGa_2O_4$ nanowires had been achieved [15–17]. Nevertheless, large-scale straight $ZnGa_2O_4$ nanowires with high purity cannot be fabricated by the methods mentioned above, which limits their applications in the electronic and optoelectronic fields. Recently, Yanagida et al. have found that carbon layer can enhance Au-catalytic VLS growth of some metal oxides nanowires including ZnO, SnO_2 and MgO [18]. We deduce that the novel insight may be applied to the growth of other metal oxides nanowires. In this paper, we successfully fabricated large-scale $ZnGa_2O_4$ nanowires on the Au catalyst and carbon layer-coated Si substrates by a facile carbothermal reduction method. The structure properties and growth mechanism of the as-synthesized nanowires were investigated in detail. In addition, the cathodoluminescence (CL) spectrum of an individual nanowire was also studied, which has not been reported before.

2. Experimental

The $ZnGa_2O_4$ nanowires were grown on the Au and amorphous carbon layers coated Si (1 0 0) substrates by using a facile carbothermal reduction method. The amorphous carbon layers with thickness of 30 nm were first deposited on Si substrates by using magnetic filed filtered ion deposition technique. Then, the carbon-coated substrates were further coated with 20 nm of Au layers using magnetron sputtering deposition instrument. The source materials were mixtures of ZnO, Ga_2O_3 and graphite with molar ratio of 1:1:2. In the experiment, the mixtures were placed at the highest temperature zone of horizontal tube furnace. The composite layer of Au and amorphous carbon-coated Si substrates were placed in the downstream. After flushed with Ar twice times to remove the remaining air, the furnace temperature was rapidly heated up to 1050 °C and then kept at the temperature for 1 h under Ar carrier gas at the flow rate of 120 SCCM. Finally, the furnace was cooled to room temperature and white product was found to deposit on the Si substrate in deposition temperature region of approximately 850–900 °C.

The crystal structure of the product was analyzed by using a rotating anode Rigaku (Tokyo, Japan) D/max-2400 X-ray diffractometer with Cu Kα radiation. The morphology of the product was characterized by Hitach (Tokyo, Japan) S-4200 field-emission scanning electron microscope (FE-SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The microstructure of the product was examined by transmission electron microscopy (TEM, Philips CM 12 at 100 kV) and high-resolution TEM (HRTEM, Philips CM 12 at 200 kV). The cathodoluminescence (CL) study of a single nanowire was performed in the scanning electron microscope equipped with an Oxford Instruments MonoCL2 spectrometer at room temperature. The focused electron beam was scanned over the surface, and the emitted light was collected

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* Corresponding author. Tel.: +86 571 86843222; fax: +86 571 86843222.
E-mail address: whtang@zstu.edu.cn (W.H. Tang).

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doi:10.1016/j.jallcom.2009.09.145

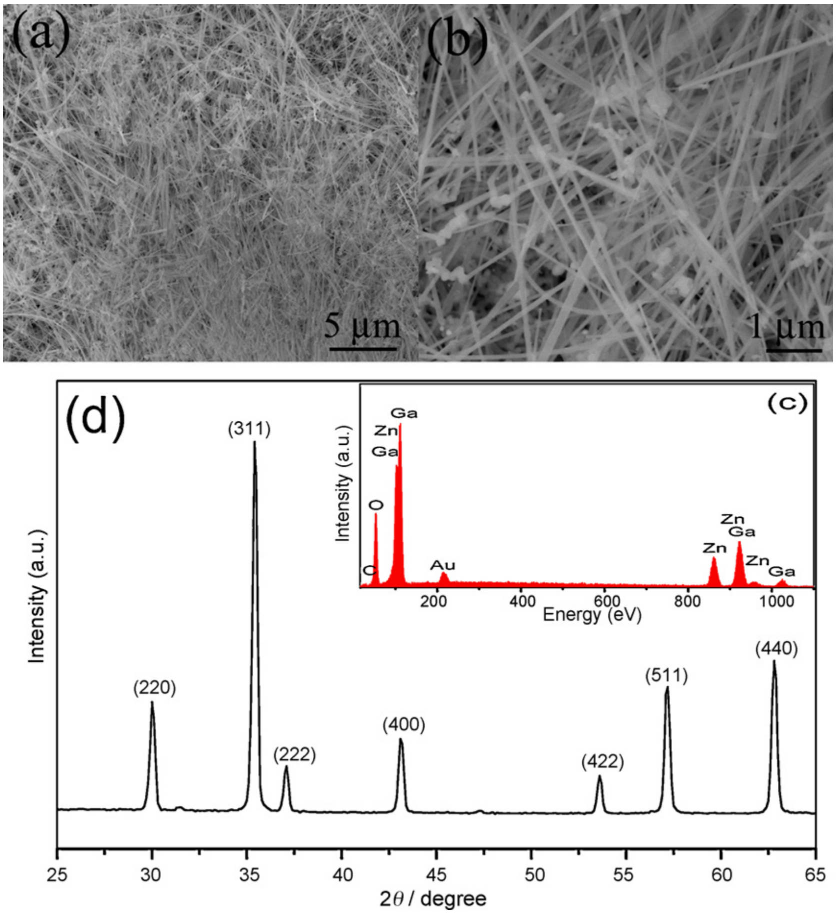

Fig. 1. (a) SEM image of the $ZnGa_2O_4$ nanowires. (b) Enlarged SEM image of the $ZnGa_2O_4$ nanowires. (c) EDS spectrum of the $ZnGa_2O_4$ nanowires. (d) XRD patterns of the $ZnGa_2O_4$ nanowires.

with a parabolic aluminum mirror and guided to the slit of a grating monochromator with a focal length of 20 cm. The measurement was conducted at an accelerating voltage of 10 kV and probe current of 200 pA.

3. Results and discussion

The morphology of the as-deposited product was first characterized by SEM. The low-magnification SEM image (Fig. 1a) clearly reveals that the product is composed of a large amount of straight nanowires with average length up to 10 µm. The enlarged image (Fig. 1b) shows that the nanowires have smooth surface and most of them have diameter of about 100–200 nm. Some nanoparticles identified as Au are observed to attach on the tip of nanowires, indicating a typical VLS growth process of the nanowires. The corresponding EDS spectrum (Fig. 1c) indicates that the nanowires mainly consist of Zn, Ga and O elements. The Au and C signals come from the Au catalyst and carbon layer predeposited on the Si substrates. Fig. 1d shows the XRD patterns of the nanowires. All the sharp diffraction peaks can be indexed as face-centered spinel-structured $ZnGa_2O_4$ with $a = 8.551$ Å, which is quite consistent with the standard data (ICDD-PDF No: 38-1240). The diffraction peaks of Au catalysts are not detected, which may be due to the instrumental resolution. Combined with the EDS and XRD results, the product can be confirmed as $ZnGa_2O_4$ nanowires with high purity.

TEM, TEM-based EDS and HRTEM were used to further provide insight to the microstructures of $ZnGa_2O_4$ nanowires. Fig. 2a shows the typical TEM image of an individual $ZnGa_2O_4$ nanowire with diameter of about 100 nm. From Fig. 2a, we can observe that the nanowire is rather straight along growth direction and has smooth surface. Au nanoparticle is found to attach on the tip of the nanowire, indicating the growth process follows a typical VLS mechanism. The composition of the nanowires can be further confirmed by the TEM-based EDS measurement. As shown in Fig. 2b, the nanowire is composed of Zn, Ga and O elements, and molar ratio of Zn and Ga is close to 1:2, further confirming the chemical formation of $ZnGa_2O_4$. The Cu and C signals come from the Cu grid, which is not related to the composition of the nanowire. The fast Fourier transformation (FFT) pattern of the nanowire recorded from [1 1 1] zone axis (Fig. 2c) is indexed and clearly indicates the perfect single-crystalline nature of the nanowire. Fig. 2d is the corresponding HRTEM image taken from the side-edge of the nanowire. A group of parallel fringes with spacing distance of 0.48 nm corresponds to $(1\bar{1}1)$ planes of FCC structure of $ZnGa_2O_4$. A thin amorphous layer is found to attach on the surface of the nanowire and no obvious bulk defects such as stacking faults or dislocations are observed, indicating the well crystalline nature of the nanowires. From the FFT pattern and HRTEM result, we determine that the nanowires are grown along unusual [1 1 0] direction, which is not consistent with the reported [1 1 1] direction [11,19].

In order to illuminate whether carbon layers plays an important role in the growth of $ZnGa_2O_4$ nanowires, we performed $ZnGa_2O_4$ nanowires grown on Si substrate in the absence of predeposited carbon layers. As shown in Fig. 3a and b, low-density $ZnGa_2O_4$ nanowires are grown on the substrate compared with those in the presence of carbon layer. Moreover, a large amount of irregular rope-like products are attached on the substrate (Fig. 3b), indicating the Au cannot act as effective catalyst in the growth of $ZnGa_2O_4$ nanowires in the absence of carbon layers. It is found that it is

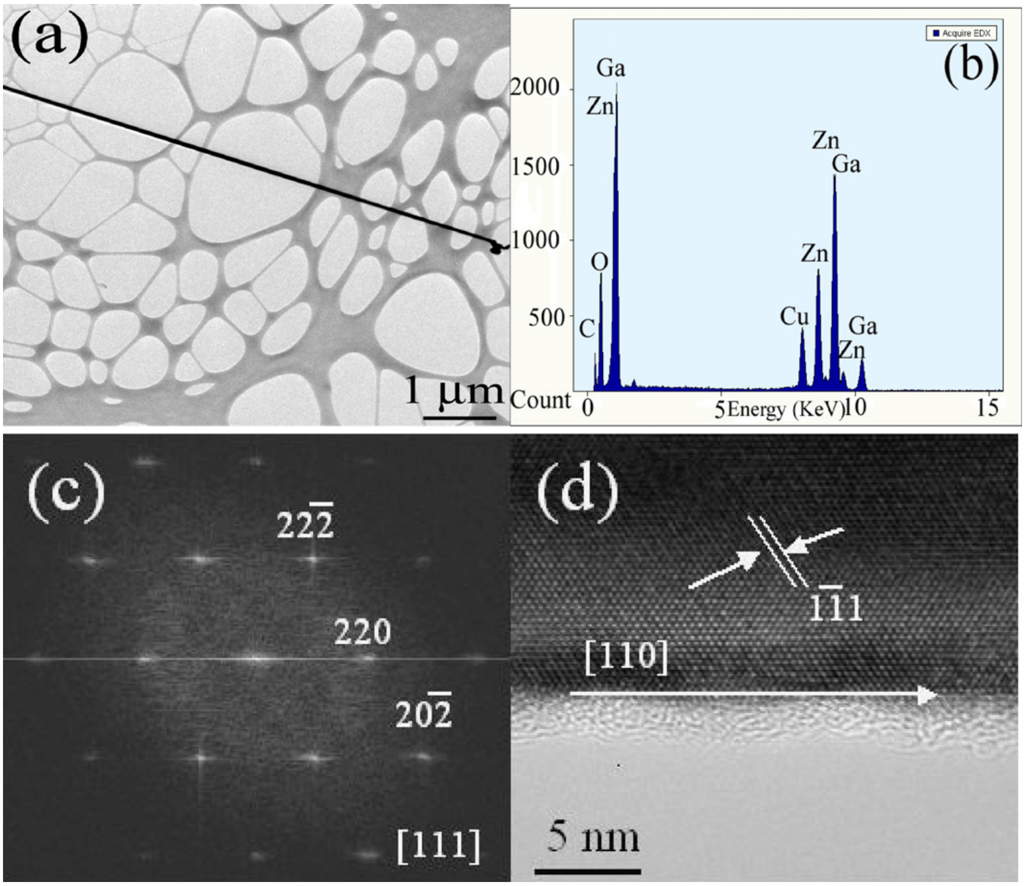

Fig. 2. (a) Typical TEM image of an individual $ZnGa_2O_4$ nanowire. (b) EDS spectrum collected from the $ZnGa_2O_4$ nanowire. (c) FFT pattern of the $ZnGa_2O_4$ nanowire. (d) HRTEM image of the $ZnGa_2O_4$ nanowire.

impossible to keep high vacuum in our experimental conditions, and part of carbon will be oxidized during the chemical vapor deposition process at high temperature. In the experiment, we observe that, if the thickness of carbon layer is too thin (below 10 nm), the carbon layer will disappear by high-temperature oxidization. Moreover, the carbon layer with thickness less than 20 nm cannot enhance the VLS process. When the thickness of carbon layer up to or more than 30 nm, the carbon layer can significantly enhance the VLS process. So, thicker carbon layer, e.g. 30 nm can enhance the VLS growth process of the $ZnGa_2O_4$ nanowires. Although the detailed role of carbon layer in the growth of $ZnGa_2O_4$ nanowires is unclear, we can confirm the carbon layers combined with Au act as effective catalysts at the initial stage of the enhanced VLS growth, which is demonstrated by SEM images shown in Fig. 3.

Fig. 4a and b displays the CL spectrum of an individual $ZnGa_2O_4$ nanowire (the morphology of the nanowire is shown in the inset of Fig. 4) and the large-scale $ZnGa_2O_4$ nanowires, respectively. As shown in Fig. 4a, only a strong and broad emission band centered at 537 nm (2.31 eV) is observed at room temperature. The band gap emission of $ZnGa_2O_4$ centered at 268–293 nm is not detected, which is rather common in the formation of $ZnGa_2O_4$. The CL spectrum of the large-scale $ZnGa_2O_4$ nanowires (Fig. 4b) reveals similar emission band centered at 543 nm. Nevertheless, visible red-shift of the emission band are observed, compared with that of the single nanowire. We also investigate CL spectra of other single nanowire, revealing the similar emission band. However, the red-shift or blue-shift of the broad emission band are also observed in the single nanowire. So, it is deduced that the CL spec-

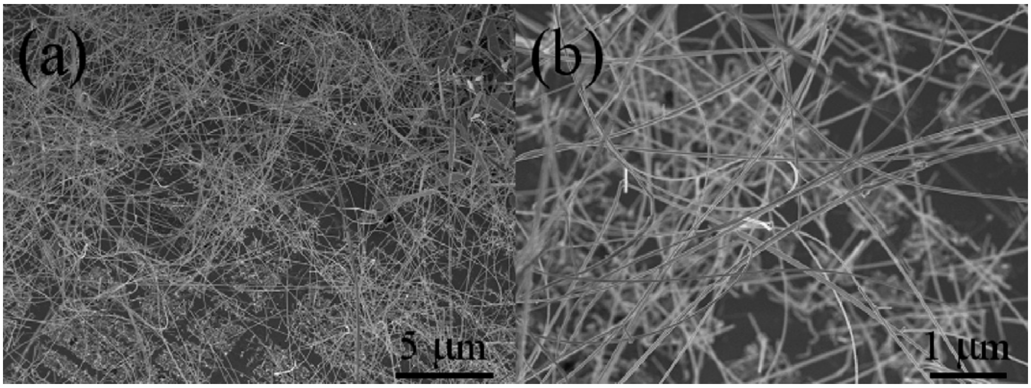

Fig. 3. (a and b) SEM and enlarged SEM image of the $ZnGa_2O_4$ nanowires in the absence of predeposited carbon layers, respectively.

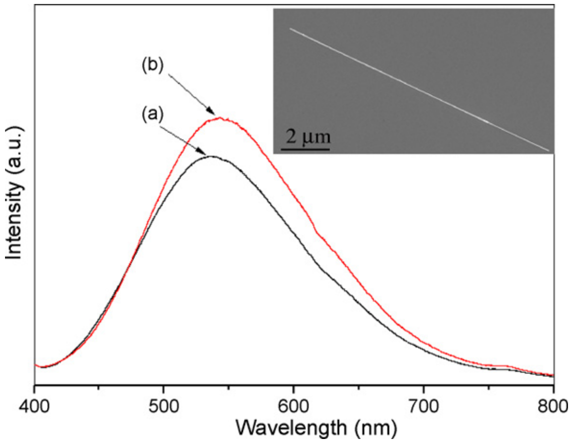

Fig. 4. Room-temperature CL spectrum of (a) a single $ZnGa_2O_4$ nanowire and (b) large-scale $ZnGa_2O_4$ nanowires. The inset is the morphology of the single $ZnGa_2O_4$ nanowire.

trum of the large-scale nanowires is summation of CL spectra of each single nanowire, and the CL mechanisms of these nanowires are same in nature. Generally, oxygen vacancies and Zn/Ga stoichiometry are the main reasons for the various emission bands of $ZnGa_2O_4$ nanowires [20–23]. Herein, we have demonstrated that the as-prepared $ZnGa_2O_4$ nanowires are close to perfect Zn/Ga stoichiometry. So, we deduce that oxygen vacancies instead of Zn/Ga stoichiometry should be responsible for the broad emission band observed here. Oxygen vacancies are the intrinsic defects in $ZnGa_2O_4$ and can capture electrons to form single ionized vacancies. These ionized vacancies can act as deep defect donors and thus form new energy levels, which further influences the optical properties of $ZnGa_2O_4$. Nevertheless, the oxygen vacancies-related CL property is rather complicated and the exact mechanism needs to be further investigated.

4. Conclusions

Large-scale $ZnGa_2O_4$ nanowires were fabricated by a facile carbothermal reduction using mixtures of ZnO, Ga_2O_3 and graphite as precursors. These high pure nanowires were single-crystalline and very straight along [1 1 0] growth direction. The growth mechanism followed an enhanced oxide vapor–liquid–solid (VLS) process. In the Au-catalytic $ZnGa_2O_4$ nanowire growth process, carbon layers predeposited on the substrates surface strongly enhance the initial stage of VLS growth. The CL spectrum of an individual nanowire clearly indicates a broad green emission band centered at 537 nm. We deduce that a large quantity of single ionized oxygen vacancies should be responsible for the unusual emission band.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (60571029, 50672088) and the Innovative Youth Team of Natural Science Foundation of Zhejiang Province (R4090058).

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