Intensive Blue Light Emission from β-Ga_2O_3 Nanowires, Nanotapes and Nanosheets by Carbothermal Synthesis

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Abstract: Gallium oxide nanowires, nanotapes and nanosheets were synthesized by carbothermal method using carbon nanotubes as reactant and characterized by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was confirmed that gallium oxide nanostructures were single crystalline. Photoluminescence (PL) spectrum of the product displayed an intensive blue light emission peak at 487 nm at room temperature.

Key words: gallium oxide; carbon nanotubes; nanostructures; photoluminescence
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1 Introduction

Monoclinic gallium oxide (β-Ga_2O_3) with a wide band gap ($E_g \approx 4.9$ eV)[1] exhibits excellent electronic and optical properties[2], and is used in optoelectronic devices and gas sensors[3]. Recently, low dimensional β-Ga_2O_3 nanostructures, such as nanowires, nanotapes and nanosheets, have attracted considerable attention due to its unique structure, exceptional properties and potential applications. Zhang *et al*[4] fabricated Ga_2O_3 nanowires using simple physical evaporation of pure metal gallium. It was also reported that GaN powder could be used as a source material for the production of Ga_2O_3 nanowires by DC arc-discharge[5]. Carbothermal approach has also been developed to obtain large scale of Ga_2O_3 nanowires[6]. Reaction between metallic Ga and H_2O was another efficient way to synthesize Ga_2O_3 nanostructures[7]. Physical evaporation of the mixed Ga-Ga_2O_3 or GaN powders could successfully produce single crystalline Ga_2O_3 nanotapes[8] and the mixtures of nanotapes and nanosheets[9]. Ga_2O_3 nanowires were potential blue and ultraviolet light emitters[6], while Ga_2O_3 nanotapes and nanosheets presented a stable blue light emission peak at 460 nm[7].

Carbon nanotube is an excellent template to synthesize nanowires by its confinement effect[10]. In this paper, carbon nanotubes are used as a reactant. β-Ga_2O_3 nanowires, nanobelts and nanosheets are found in the product, and PL properties have been characterized.

2 Experimental

In a typical procedure, gallium oxide powder was mixed with multi-wall carbon nanotubes prepared by pyrolysis of acetylene[11] with the weight ratio of 1:1~1:1.5. The mixture was charged in a ceramic vessel covered by a piece of molybdenum plate to keep a high gallium oxide vapor pressure during the reaction process. The vessel was then placed at the center of a quartz tube fixed in a horizontal furnace. The furnace was heated up to 950℃~980℃ in 30 minutes and ran for 2 h~4 h in nitrogen atmosphere. After the furnace was cooled down to room temperature, white fluffy product was collected from the inner surface of the vessel and Mo plate.

The general morphology of the product was observed by SEM. X-ray diffraction (XRD) was performed using CuK_α radiation. TEM observation and selected area electron diffraction (SAED) were carried out using Philips CM200 operated at 200 kV. X-ray energy dispersive spectrum (EDS) was performed by EDAX equipped in the TEM. PL spectra were carried out in a fluorescence spectrophotometer at room temperature.

3 Results and Discussion

The general morphology of the product formed on molybdenum plate is shown in Fig.1. The product consists of nanowires and nanosheets, as shown in Fig.1a.

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Fig.1b shows a curved nanotapes at a high magnification. Most of nanotapes are curved, it is suggested that they are elastically flexible.

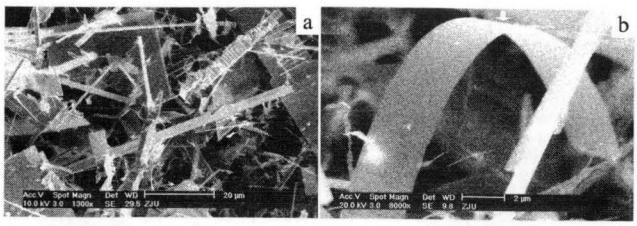

Fig.1 SEM images of nanowires, nanosheets (a) and nanotapes (b)

Fig.2 displays TEM images of as-synthesized nanostructures. Some straight nanowires with diameter ranging from 60 nm to 100 nm and length up to tens of micrometers are shown in Fig.2a. All nanowires are homogeneous without nanoparticles at tips, supporting the expectation that no other metal nanoparticles helped to catalyze the observed nanowire growth, which suggests a different growth mechanism from vapor-liquid-solid (VLS)[11]. Some thin nanosheets are also presented in Fig.2a and their thickness is estimated to be tens of nanometer. The inset in Fig.2a is a SAED pattern of a single nanowire, which confirms that the nanostructures are single crystal. Fig.2b shows several nanowires, nanotapes and nanosheets. The ripple-like contrast in the thin tapes is due to the residual strain in the curved tapes. On the other hand, microtwins were found in some nanowires, as shown in Fig.2c. It shows a zigzag nanowire with a diameter around 400 nm, and one

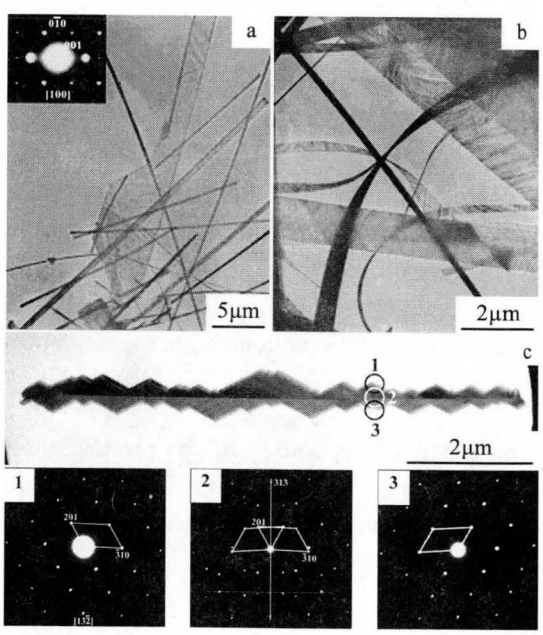

Fig.2 TEM images of Ga_2O_3 nanostructures(a, b)and a zigzag nanowire (c)

set of SAED patterns corresponding to marked circle areas 1 to 3. SAED patterns of area 1 and 3 appear to have mirror-symmetry with identical parameters. While the SAED pattern of area 2 is a superimposition of these from area 1 and 3 with a small angle deviation that may be caused by crystal structure. It is proved that area 2 covered a twin boundary and it was located between area 1 and 3. Similarly, some symmetric twinnings were also observed in high-resolution TEM of Ga_2O_3 nanowires[4]. The twinning structures could play important roles for the growth of nanowires via a vapor-solid (VS) process[4]. The EDS analysis confirms the presence of gallium, oxygen, carbon, and copper, where elements C and Cu came from the carbon coated copper grid. The EDS result implies that these nanostructures are gallium oxide.

The XRD pattern of the product (in Fig.3) is recorded with Mo plate. Most of the diffraction peaks (indicated by solid triangles) can be indexed to be a monoclinic phase peak, which is consistent with bulk β-Ga_2O_3 (PDF No. 41-1103). The relative intensity of the peaks differs from that of bulk Ga_2O_3, which result from the formation of nano-sized structures. No crystalline phases other than Mo (indicated by solid circles) that was used as superstratum in the experiments were found within the detection limit. Hence, the as-synthesized products are pure. It is proved that carbon nanotubes only act as a reactant and have not been introduced into the sample.

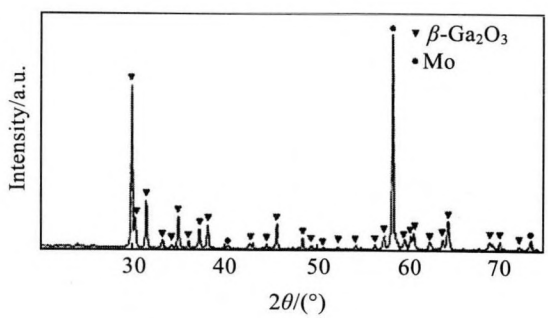

Fig.3 XRD pattern of as-synthesized sample on Mo plate

The various morphologies of Ga_2O_3 nanostructures imply that carbon nanotube-confined reaction can not occur here[10]. The chemical reactions are ascribed to a carbothermal process[6]. There are several growth mechanisms developed to explain one-dimensional growth. One is VLS process[11], in which metal nanoparticles as catalyst were capped at the tip of nanostructures. The other is VS mechanism[12], in which nanostructures were fabricated from the vapor of precursor directly without a liquid state. For the Ga_2O_3 nanostructures synthesized in

our cases, VS mechanism is dominant, because no catalysts were involved and observed. The growth process herein may be as follows. Carbon atoms from carbon nanotubes firstly react with powdered Ga_2O_3 to form Ga_2O and Ga vapor. The resultant vapor is transformed into Ga_2O_3 by oxygen oxidization[6], where oxygen might come from silicon oxide on the surface of the ceramic vessel[4], then Ga_2O_3 deposits and aggregates into many nuclei. These nuclei act as seeds for the growth of nanostructures[6].

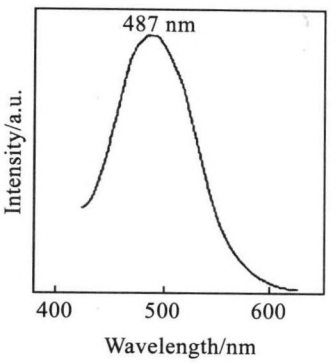

Fig.4 PL spectrum of Ga_2O_3 nanostructures at room temperature

PL spectrum of Ga_2O_3 product presented in Fig.4 is detected with excitation wavelength of 377 nm at room temperature. Only a broad peak centered at 487 nm (belong to blue light range) can be activated. As an excellent material for blue photoluminescence, Ga_2O_3 has been intensively studied. Harwig and Kellendouk once proposed that the blue emission was due to the recombination of an electron on a donor formed by oxygen vacancies and a hole on an acceptor formed by gallium vacancies[13]. Vasil'stiv *et al.* suggested that the acceptor should be formed by a gallium-oxygen vacancy pair[14]. For the present Ga_2O_3 nanostructures, a huge number of oxygen vacancies and gallium-oxygen vacancy pairs may be formed readily. It should be put forward that in some investigations on photoluminescence of gallium oxide crystal or nanowires, not only blue but also ultraviolet emission has been found[2,6]. However, in the recent report[7] and our work, only blue emission peak has been detected for nanostructures including nanobelts and nanosheets.

4 Conclusions

β-Ga_2O_3 nanowires, nanotapes and nanosheets can be synthesized by carbothermal route. The growth of these nanostructures belongs to a VS mechanism. PL spectrum at room temperature shows an intense blue light emission at 487 nm.

References

[1] Tippins H H. *Phys Rev*[J], 1965, 140: A316
[2] Binet L, Gourier D. *J Phys Chem Solids*[J], 1998, 59: 1241
[3] Ogita M, Saika N, Nakanishi Y *et al. Appl Surf Sci*[J], 1999, 142: 188
[4] Zhang H Z, Kong Y C, Wang Y Z *et al. Solid State Commun*[J], 1999, 109: 677
[5] Park G S, Choi W B, Kim J M *et al. J Crystal Growth*[J], 2000, 220: 494
[6] Wu X C, Song W H, Huang W D *et al. Chem Phys Lett*[J], 2000, 328: 5
[7] Dai L, Chen X L, Zhang X N *et al. J Appl Phys*[J], 2002, 92: 1062
[8] Pan Z W, Dai Z R, Wang Z L. *Science*[J], 2001, 291: 1947
[9] Dai Z R, Pan Z W, Wang Z L. *J Phys Chem B*[J], 2002, 106: 902
[10] Cheng J P, Zhang X B, Liu F *et al. Carbon*[J], 2003, 41: 1965
[11] Sun Y L(孙沿林), Zhang X B(张孝彬), Ning Y S(宁月生) *et al. J Inorg Mater*(无机材料学报)[J], 2002, 17: 337
[12] Wang M X(王明显), Yang L(杨 利), Wang C M(王翠梅) *et al. Rare Metal Materials and Engineering*(稀有金属材料与工程) [J], 2004, 33(6): 670
[13] Harwig T, Kellendonk F. *J Solid State Chem*[J], 1978, 24: 255
[14] Vasil'stiv V I, Zakharko Ya M, Prim Ya I. *Ukr Fiz Zh*[J], 1988, 33: 1320

碳热法合成具有蓝光发射特性的氧化镓纳米线、纳米带和纳米片

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摘 要：利用碳纳米管通过碳热法合成了氧化镓纳米线、纳米带和纳米片。采用扫描电镜和透射电镜对其进行了形态和结构表征。合成的氧化镓纳米结构是单晶体。室温光致发光谱分析发现，氧化镓纳米晶在蓝光区域 487 nm 处产生明显的发射峰。

关键词：氧化镓；碳纳米管；纳米结构；光致发光谱

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