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Structure and Photoluminescence Properties of β-Ga2O3 Nanofibres Synthesized via Electrospinning Method

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Abstract: This paper reported the β-Ga2O3 nanofibres which fabricated by electrospinning, and then calcining in oxygen at 750, 850, 950 and 1050°C. The structure and properties of β-Ga2O3 nanofibers have been studied though kinds of methods such as XRD, Photoluminescence (PL) spectrum, Raman spectrum, Scanning electron microscope (SEM) and FT-IR. The diameters of these nanofibres are from 60 to 130nm and the lengths of these nanofibres are about couple millimetres. The spectrum of PL which excitation at 365nm gave us the information that the emission peak of these β-Ga2O3 nanofibres is about 470nm, it may be coursed by the various defects including the vacancies of gallium and oxygen and the gallium-oxygen vacancy pairs as well, and observed that with the increasing of the annealing temperature, the emission peaks have a small bule swifting, and the crystallinity become better at the same time.

1. Introduction

β-Ga2O3 is a very important semiconducting material [1], and it has kinds of crystalline structures called α, β, γ, δ and ε phases. It has a band gap of 4.9 eV [2]. Nanosize β-Ga2O3 owns special properties of conduction and semiconductor which indicate applications in the devices of optoelectronic such as flat panel displays, photoelectric converter, and Optical limiter for UV oxide because of its surface area/volume ratio [3]. It also can be used to fabricate solar-blind devices due to its solar-blind properties under deep ultraviolet environment [4-8]. And the bigger surface area/volume ratio is the better for the application of gas sensors. Such as S.H.Park, et al. [9] observed CO gas sensing properties through synthesis surface nitriding Ga2O3 nanowires. And Shinji Nakagomi, et al.[10] found that the sensors fabricated by a β-Ga2O3 thin film could detect 100ppm H2 in 20% O2/N2 at 400°C. Therefore, it is necessary to get nanostructure β-Ga2O3. Now days, β-Ga2O3 of nanostructure could be synthesized by several kinds of methods like simple precipitation technique [11], electrochemical reaction [12], atmospheric-pressure CVD [13], metal organic chemical vapor deposition (MOCVD) [1], and thermal evaporation method[14]. But, these methods need complicate equipments, catalysis, or introduce impurity atom, and the prepared β-Ga2O3 including the vestigital of the catalysis [15]. Therefore, it is necessary to fabricate β-Ga2O3 nanofibres which have a high purity. However, there are no reports on the effect of annealing temperature on the structure, photoluminescence properties and purity of β-Ga2O3 nanofibres by electrospinning. In this paper, a kind of simple and reliable method of fabricating β-Ga2O3 nanofibres is recommended—electrospinning. Electrospinning is a simple and less costly method to synthesis nanofibers with high draw ratio. Kinds of nanofibres of materials could be generated with it including

polymer, polymer or inorganic composites, and inorganic nanofibres. Through sintering of the as-prepared compound fibers carefully, β-Ga2O3 nanofibres have been fabricated successfully.

2. Experiment

Ga2O3 nanowires were electrospun from precursor which was prepared by the solution of Ga(NO3)3·6H2O, and polyvinylpyrrolidone(PVP, Sigma Aldrich, Mw≈1300000), PVP is an aggregation of composite materials because it has good ethanol and water solubility and the compatibility with nitrate. The precursor solution containing 1.0g Ga(NO3)3, 6.5 ml C2H5OH, 5.5 ml H2O, and 4.0 g PVP respectively. And then the solution was stirred for 12h directly. After that, the viscous solutions was obtained. Then the viscous solution was put into a injector with a hollow needle, The process of electrospinning was shown in Figure. 1. Positive pole of a high-voltage power supply and the point of the syringe needle were concatenated while the negative pole was connected to the plate of the collector. Voltages connected to the tip and the collector plate was 15 kV and -15KV respectively, and the distance between the needle tip and the collector was 25 cm. After all these parameters were set up, the solution would be electrospun next. The deposition continued for 1h so that the dense mats would be well obtained. After spinning, the fibers which prepared would be dried at 80°C for 3h. And then the fibres would be calcined at different temperatures to get different samples.

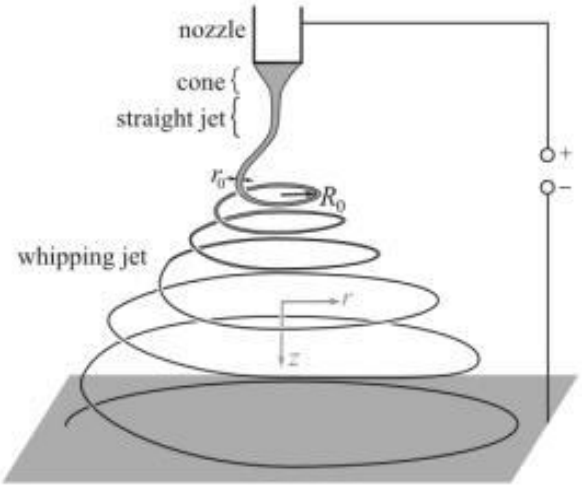

Figure1. Process of electrospinning

The crystalline structure of the fibres were examined by X-ray diffraction (XRD) using General motors XD-3 with Cu target. Raman spectrum were detected on a Horiba jobin yvon T64000 Confocal Raman spectrometer using 532nm excitation laser. The FT-IR spectrum has been detected during the range of 4000-400 cm-1 with a Bruker Vertex 80V FTIR spectrometer instrument. The morphology of the nanofibers were characterized by the SEM(JSM-6510). The photoluminescence (PL) spectra were measured at room temperature with a Edinburgh FLSP920 spectrophotometer. The excitation light was the monochromatic light from a Xenon short Arc lamp with a wavelength of λ=365nm.

3. Result and Discussion

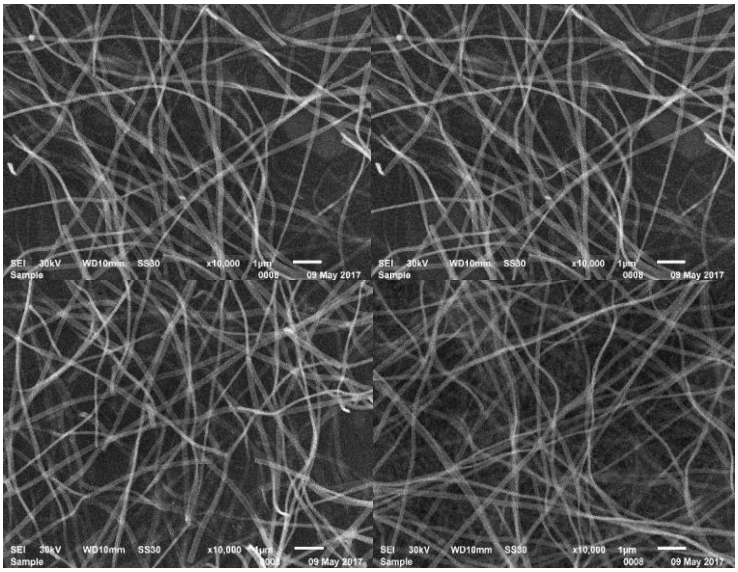

Figure. 2. SEM images of the β-Ga2O3 calcined nanofibres at : (a)750°C, (b) 850°C, (c) 950°C, (d) 1050°C

Figure.2 shows the typical SEM images of the β-Ga2O3 nanofibers which calcined at different temperatures and the annealed fibres are distribution randomly. And the surface of the fibres is very slick. There are several factures in the 850°C and 950°C samples maight be caused by the evaporation of the solvent, There are no great particles attached on the surface of the nanofibres. And, the width of the fibres is in the range of 60nm-200nm, and the average diameter of the β-Ga2O3 nanofibres is about 120nm. And the length are several micrometers. It is observed that the calcined temperature do not have an obvious effect on both the surface topography and the crystalline phase of the fibres.

Figure. 3 shows the XRD pattern of β-Ga2O3 nanofibres which annealed at 750, 850, 950, 1050 °C. The lattice constants of the crystalline phase are a0 = 1.2227 nm, b0 = 0.3039 nm, c0 = 0.5808nm. All the peaks are matched well to β-Ga2O3 and the peaks are (201), (-202), (020) respectively [16]. The XRD pattern signs that the annealed nanofibres was β-Ga2O3 surely. And with the increasing of the annealing temperature, all the peaks become higher and sharper indicate a higher degree of crystallization. No other impurity phases are detected, so the samples we obtained were pure without other dephasigns.

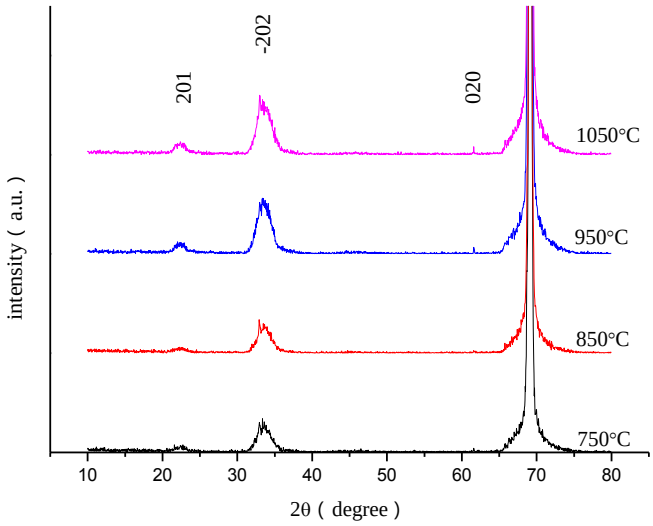

Figure 3. XRD pattern of β-Ga2O3 nanofibres annealed at 750, 850, 950, 1050 °C

Figure.4 shows the PL spectrum of the β-Ga2O3 nanofibres annealed at 750, 850, 950, 1050 °C respectively under excitation of 365nm. The dominant emission located at approximately 470 nm in the blue region. And the emission (470 nm) of blue band may be produced by the recombination of an electron of a donor originate from oxygen vacancies (VO) and a hole from an acceptor originate from gallium vacancies (VGa) or the gallium-oxygen electron hole pair (VO, VGa) [17][18]. It is reported that the peaks of the blue emission will enhance with the increase of the gallium-oxygen vacancy pairs [16][19]. Figure.4 shows that the blue emission peaks decrease with the increase of the annealing temperature. It may result from the reduce of the gallium-oxygen vacancy pairs caused of the reacting between O2 and as-prepared samples more fully. As for the blue shift of the emission spectrum, it probablely results of the quantum size effect [20] caused by the small tapering off of the nanowires which cannot be observed easily.

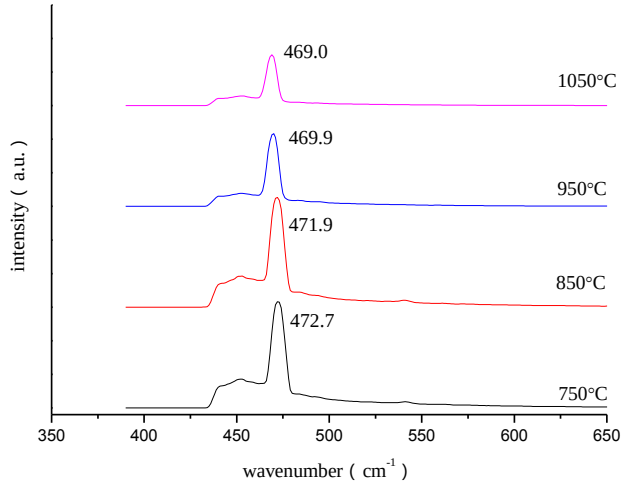

Figure 4. PL spectrum of the β-Ga2O3 nanofibres annealed at 750, 850, 950, 1050 °C

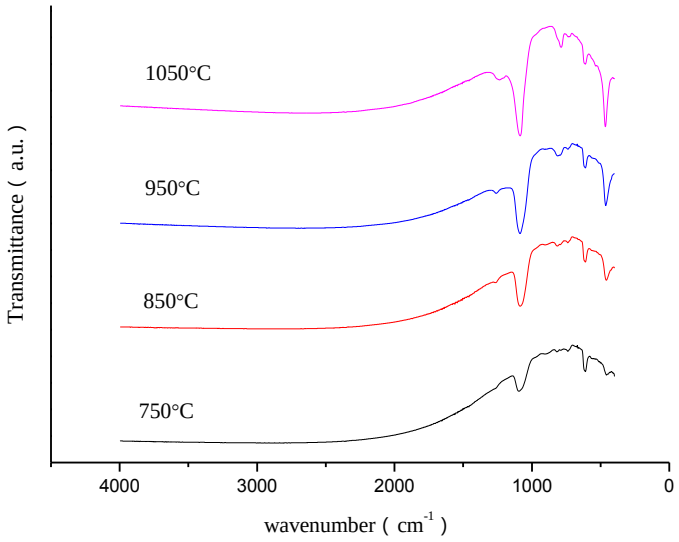

Figure 5. FT-IR spectrum of the β-Ga2O3 nanofibres calcined at 750, 850, 950, 1050 °C

The peaks located at 613 and 459 cm^{-1} in Figure.5 assigned to Ga–O–Ga and Ga–O vibration of β-Ga2O3 respectively, instead of 650 and 480 cm^{-1} of the peaks in the α-Ga2O3 [21]. and the peak at 1089 cm^{-1} belongs to asymmetric stretching vibration absorption of Si-O-Si [22]. it's obviously observed that with the increase of the annealing temperature, the infrared absorption is becoming stronger which indicated that the content of Ga–O–Ga and Ga–O increased. It signify that with the increase of the annealing temperature, oxygen vacancies were filled with oxygen elements to form Ga–O–Ga and Ga–O bonds.

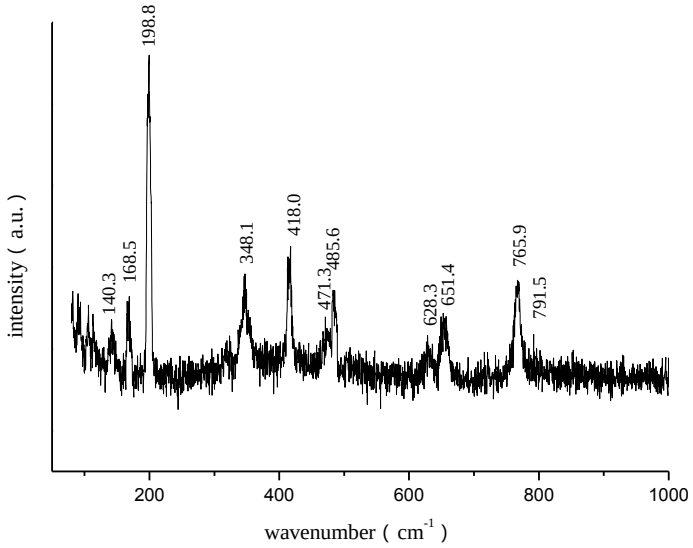

Figure 6. Raman spectrum of β-Ga2O3 nanofibres

Figure. 6 shows typical micro-Raman spectra of β-Ga2O3 nanofibres. The Raman spectra show 11 clear Raman peaks. And the positions of the peaks locate at 140.3, 168.5, 198.8, 348.1, 418.0, 471.3, 485.6, 628.3, 651.4, 765.9, 791.5 (cm^{-1}). These peaks are very peaked and narrow which sign that the crystallinity is very well and these peaks belong to the C2h group symmetry, implying a unit cell with two formula units, Ga2O6 octahedra and GaO4 tetrahedra [16]. The peaks of the Raman spectrum can be divided into three kinds such as low (below 200 cm^{-1}), mid (between 300 $cm^{-1}$and 500 cm^{-1}), and high (between 500 cm-1and 800 cm^{-1}) frequency modes. The low modes are related to the low-frequency libration and translation of tetrahedron–octahedron chains [23]. The mid modes are relate to the mid-frequency deformation of Ga2O6 octahedra. The last high modes attributed to the high frequency and result of stretching and bending of GaO4 tetrahedra [24].

4. Conclusion

In summary, we have studied the structure and photoluminescence properties of β-Ga2O3 which synthesized via electrospinning. SEM show the Morphology of the fibres, XRD and Raman confirmed the monoclinic phase of β-Ga2O3 nanowires, indicate that the samples we fabricated are pure. The PL spectrum of the β-Ga2O3 nanofibres exhibits the blue emission peaks about 470nm under excitation of 365nm at room temperature and the mechanisms of the blue shift and photoluminescence of the β-Ga2O3 nanofibres were discussed. FT-IR spectrum indicated that oxygen vacancies decreased with the annealing temperature increasing.

5. Acknowledgment

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6. Reference

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