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# Growth and properties of one-dimensional β-$Ga_2O_3$ nanostructures on c-plane sapphire substrates

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ABSTRACT

One-dimensional β-$Ga_2O_3$ nanostructures were grown at different temperatures on c-plane sapphire substrates by MOCVD using Au as catalyst. The structural, morphological and photoluminescence properties of β-$Ga_2O_3$ nanostructures grown at different temperatures were characterized and compared in detail. As the growth temperature was increased, β-$Ga_2O_3$ nanostructures exhibited improved crystalline quality and possessed a typical β-$Ga_2O_3$ structure with high purity. The β-$Ga_2O_3$ nanostructures grown at 750 °C showed intense ultraviolet-blue emission at room temperature. Different morphologies including islands-like, nanowires, nanorods, grain-like structures were obtained depending on the growth temperature. The correlation between the nanostructures shapes and the growth processes was also discussed.

## 1. Introduction

Gallium oxide ($Ga_2O_3$) has five crystalline polymorphs: α, β, γ, δ and ε phase. Among all of these phases, the most stable one is β-$Ga_2O_3$, which exhibits monoclinic crystal structure [1–3]. Due to its excellent thermal and chemical stability at high temperature, wide band gap of about 4.9 eV at room temperature and high breakdown electric field of 8.0 MV/cm, β-$Ga_2O_3$ shows promising applications in various devices, such as flat panel displays, UV detectors, field effect transistors and high-temperature gas sensors [4–8]. Recently, in order to improve the device performance effectively, one-dimensional β-$Ga_2O_3$ nanostructures including nanowires, nanorods, nanotubes and nanobelts, which have large surface to volume ratio and high surface states density, have attracted considerable attentions of researchers owing to their novel structural and optoelectronic properties as compared to bulk [9–11]. Many methods have been applied to grow one-dimensional β-$Ga_2O_3$ nanostructures such as chemical vapor deposition [12], thermal evaporation [13], arc-discharge [14], metal organic chemical vapor deposition (MOCVD) [15] and hydrothermal process [16]. Among these methods, one-dimensional nanostructures have been obtained by either catalyst-free or catalyst-induced technique [15,17,18]. However, the morphologies and properties of nanostructures have presented difference completely. Calestani et al. investigated the properties of β-$Ga_2O_3$ nanowires obtained by thermal evaporation on not-catalyzed and catalyzed substrates. They found that $Ga_2O_3$ was deposited much less on not-catalyzed substrates rather than on catalyzed ones. Catalyst could promote a homogeneous and dense distribution of nanostructures on the substrates. And compared with the samples grown without catalyst, a stronger increase in luminescence intensity was observed on samples grown with catalyst [19]. The shapes and properties of the nanostructures are known to be affected by the growth processes strongly, particularly when the catalysts are used. However, to the best of our knowledge, there are not enough details on the relationship between the nanostructures shapes and the growth processes so far [19,20]. Therefore, the studies focused on shape-controlled growth are necessary. The studies on correlation between the nanostructures shapes and the growth processes will provide important and effective information for the manufacture of β-$Ga_2O_3$ nanostructures devices.

In this paper, one-dimensional β-$Ga_2O_3$ nanostructures were grown on c-plane sapphire substrates by MOCVD using Au as catalyst. The structural, morphological and photoluminescence (PL) properties of β-$Ga_2O_3$ nanostructures grown at different temperatures were investigated in detail. In addition, the correlation between the nanostructures shapes and the growth processes was also discussed.

## 2. Experimental

The β-$Ga_2O_3$ nanostructures were grown on Au catalytic c-plane sapphire substrates by MOCVD. Prior to the growth process, the substrates were cleaned successively by acetone, alcohol, deionized water, and then dried with $N_2$. Firstly, a 2-nm-thick Au film was deposited on the sapphire substrates by thermal evaporation technique. In order to obtain Au nanoparticles, the Au coated substrates were annealed at temperature of 600 °C for 1 h in $N_2$ environment. Then, the β-$Ga_2O_3$

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nanostructures were grown on the Au nanoparticles coated substrates by MOCVD. Trimethylgallium (TMGa) and $O_2$ were used as Ga and O sources, respectively. High purity Ar was used as carrier gas and flowed through the TMGa bubbler, which was maintained at 5 °C. The flow rate of Ar carrier gas was controlled at 20 sccm. And $O_2$ with a flow rate of 400 sccm was introduced into the chamber. During the growth process, the growth pressure was kept at 10 mbar. The growth temperature was varied from 600 °C to 750 °C (600 °C, 650 °C, 700 °C, 750 °C).

The crystal structures of β-$Ga_2O_3$ nanostructures were investigated by X-ray diffractometer (XRD, Rigaku Ultima IV). Raman spectra were recorded at room temperature on a micro-Raman spectrometer (Renishaw) using a wavelength of $\lambda$ = 514 nm $Ar^+$ laser. Field emission scanning electron microscopy (FESEM, SIGMA HD) equipped with energy dispersive X-ray spectroscopy (EDX) was used to perform the surface morphology and elemental analysis of the β-$Ga_2O_3$ nanostructures. The PL spectra were measured by a Horiba iHR550 spectrometer with a 220 nm YAG laser as excitation source at room temperature.

## 3. Results and discussion

In order to investigate the phase structure and crystallinity of β-$Ga_2O_3$ nanostructures, XRD measurements are performed. Fig. 1 shows the XRD patterns of β-$Ga_2O_3$ nanostructures grown at different temperatures on the Au catalytic sapphire substrates. Except the diffraction peaks of $Al_2O_3$ substrate (006) and Au, no other diffraction peaks are found for the growth temperatures of 600 °C and 650 °C, indicating that the β-$Ga_2O_3$ nanostructures are amorphous. With increasing the substrate temperature above 700 °C, as shown in Fig. 1, many sharp diffraction peaks matched well with β-$Ga_2O_3$ appear, which are in agreement with the Joint Committee on Powder Diffraction Standards card (JCPDS, No. 43-1012) [21]. For the β-$Ga_2O_3$ nanostructures grown at 700 °C, strong diffraction peaks indexed as ($\bar{2}$01) and ($\bar{6}$03) plane and some weak peaks indexed as (400), (002), (111), (512) plane, etc. are observed from Fig. 1, which indicates that most of the β-$Ga_2O_3$ nanostructures have ($\bar{2}$01) preferred growth orientation. The appearance of sharp peaks indicates that crystalline quality of β-$Ga_2O_3$ nanostructures is improved due to the larger energy provided during the nanostructures growth procedure at higher temperature. The relative peak intensity is related to the growth direction. When the growth temperature is increased to 750 °C, no particular preferred orientation is identified. The results are also confirmed by the following surface morphology studies. No other phases of $Ga_2O_3$ or impurities related diffraction peaks are observed. Thus, the XRD results reveal that the $Ga_2O_3$ nanostructures are single phase β-$Ga_2O_3$ with high purity.

For further investigating the structural properties of β-$Ga_2O_3$ nanostructures, Raman measurements are carried out, as shown in Fig. 2. For the β-$Ga_2O_3$ nanostructures grown at 600 °C and 650 °C, all the Raman peaks observed in the spectra are due to the $Al_2O_3$ substrates. The peaks related to β-$Ga_2O_3$ nanostructures are not visible. It is well known that Raman peaks will broaden due to the disorder in the materials. The $Ga_2O_3$ nanostructures grown below 650 °C do not present any Raman peaks, which is attributed to poor crystalline quality [22]. The Raman spectrum of β-$Ga_2O_3$ nanostructures grown at 700 °C shows many Raman peaks. All the peaks are associated with β-$Ga_2O_3$, which indicates the formation of pure β-$Ga_2O_3$ nanostructures [23,24]. According to the previous reports [25], the β-$Ga_2O_3$ exhibits 15 Raman and 12 infrared active modes. The three main categories of Raman active modes are the low frequency modes (below 200 $cm^{-1}$) due to libration and translation of the tetrahedral-octahedra chains, the mid frequency modes (500–300 $cm^{-1}$) due to deformation of $GaO_6$ octahedra and the high frequency modes (770–500 $cm^{-1}$) due to stretching and bending of $GaO_4$ tetrahedra. It can be seen from Fig. 2 that peaks at 144.2 ($B_g$), 168.9 ($A_g$) and 200.6 ($A_g$) $cm^{-1}$ are attributed to libration and translation of the tetrahedral-octahedra chains. The peaks such as 321.0 ($A_g$), 346.9 ($A_g$), 415.7 ($A_g$) and 473.9 ($B_g$) $cm^{-1}$ are related to deformation of $GaO_6$ octahedra, while other peaks at 629.2 ($A_g$), 654.2 ($B_g$) and 767.0 ($A_g$) $cm^{-1}$ are assigned to stretching and bending of $GaO_4$ tetrahedra. With increasing the growth temperature, all the Raman peaks show remarkable enhancement, which are related to better crystallinity of the β-$Ga_2O_3$ nanostructures. Compared with large shifts of Raman peaks in previous studies [24,25], small shifts of Raman peaks are observed for the obtained β-$Ga_2O_3$ nanostructures in this study. This indicates smaller strain and lower defect density of the β-$Ga_2O_3$ nanostructures [26]. Based on above results, we can conclude that the β-$Ga_2O_3$ nanostructures have good crystalline quality.

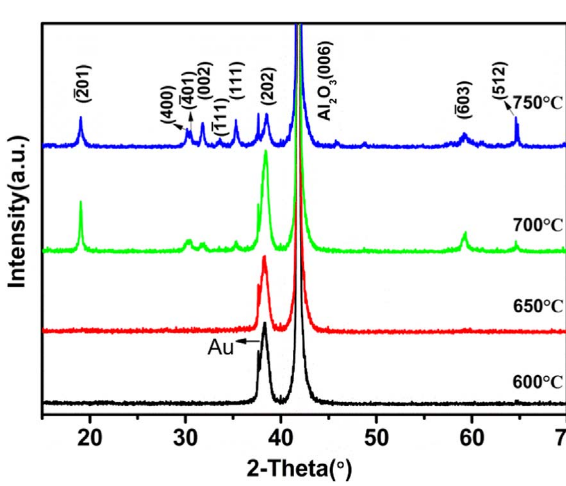


**Fig. 1.** XRD patterns of β-$Ga_2O_3$ nanostructures grown at different temperatures.

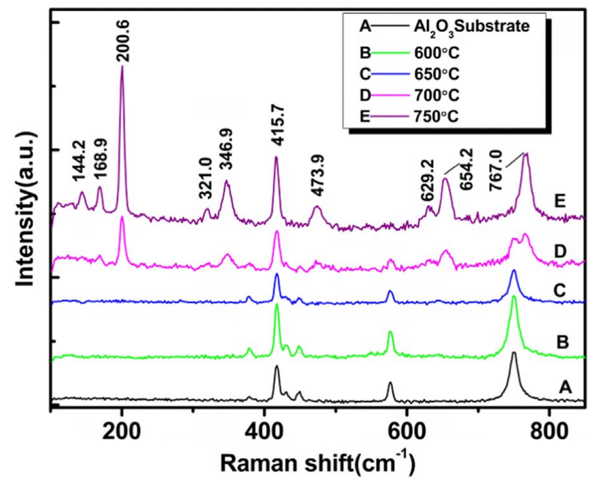


**Fig. 2.** Raman spectra of β-$Ga_2O_3$ nanostructures grown at different temperatures.

FESEM analysis is conducted to study the relationship between the β-$Ga_2O_3$ nanostructures shapes and the growth processes. Fig. 3(a) represents surface FESEM image of the Au film after annealing at 600 °C for 1 h in $N_2$ environment. It can be observed that Au nanoparticles with the diameters of about 30 nm are formed after annealing. These nanoparticles can serve as reactive sites for guiding the growth of β-$Ga_2O_3$ nanowires. FESEM images of the β-$Ga_2O_3$ nanostructures grown at different temperatures on the Au catalytic substrates are shown in Fig. 3(b)–(e) and obvious differences in the surface morphology are observed. The insets show the high-magnification images. In the case of sample grown at 600 °C, surface islands with size of about 65 nm spread over the entire substrate surface, as noted in Fig. 3(b). As the growth temperature is increased to 650 °C, surface features change from islands to nanowires structures. This can be ascribed to sufficient vapors formed in gas phase at the higher temperature. From Fig. 3(c), we can see clearly that randomly distributed β-$Ga_2O_3$ nanowires with uniform