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**Growth behavior of $\beta$-Ga$_2$O$_3$ nanowires synthesized by chemical vapor deposition**

Lei Shang $^{1,4}$, Yiqian Wang $^{2,4}$, Meiling Zhuang $^{1}$, Bing Liu $^{1}$, and Feng Shi $^{1}$

1. Textile & Clothing Institute, Qingdao University, No. 308 Ningxia Road, Qingdao, 266071, People’s Republic of China
2. The Cultivation Base for State Key Laboratory, Qingdao University, No. 308 Ningxia Road, Qingdao 266071, People’s Republic of China
3. College of Physics and Electronics, Shandong Normal University, Jinan 250014, People’s Republic of China
4. Authors to whom any correspondence should be addressed.

E-mail: shanglei_79@163.com, yqwang@qdu.edu.cn, zmlqdu@126.com, bing_liu@qdu.edu.cn and sf751106@sina.com.cn

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**Abstract**

Gallium oxide (Ga$_2$O$_3$) nanowires deposited on Si substrates were synthesized by chemical vapor deposition (CVD) of Ga powders with assisted catalyzed by nickel chloride (NiCl$_2$). The microstructure of these nanowires was investigated using high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS). Four major types of morphology were observed for these Ga$_2$O$_3$ nanomaterials, namely, the particle-fused nanowires, single-crystal nanowires, nanorods and core–shell nanowires. EELS indicated that the amorphous shell was Ga$_2$O$_3$. Because metal catalysts were introduced in the growth process, a vapor-solid (VS) growth mechanism was proposed to explain the single crystal Ga$_2$O$_3$ nanowires.

**1. Introduction**

In recent years, the preparation of one-dimensional (1D) single-crystalline conducting oxide nanomaterials has drawn much attention due to their size, morphology-related properties, and their emerging applications in functional nanodevices [1–7]. Monoclinic gallium oxide ($\beta$-Ga$_2$O$_3$) as a wide-band gap, transparent, conducting oxide (TCO) ($E_g = 4.9 \text{ eV}$), has great potential applications in optoelectronic nanodevices and gas sensors [8–13]. Although various methods have been used to prepare $\beta$-Ga$_2$O$_3$ nanomaterials such as physical evaporation [14–16], thermal chemical vapor deposition (CVD) [17, 18], arc-discharge [19], pulse laser deposition (PLD) [20], microwave plasma [21], and carbon thermal reduction [22–25], but so far, the most widely used method is CVD, which has the advantages of flexibility, simple equipment, convenient operation and maintenance, high production efficiency, high output and low pressure required for processing. However, there are few papers on the synthesis of gallium oxide nanowires using nickel chloride (NiCl$_2$) as catalyst during a thermal CVD method. Chun et al. [26] and Chang et al. [27] have reported the preparation of Ga$_2$O$_3$ nanowires using Ni as a catalyst. Also, the growth of Ga$_2$O$_3$ nanowires has not been systematically studied yet.

In this paper, $\beta$-Ga$_2$O$_3$ nanowires that were successfully synthesized on silicon substrate by CVD method will be discussed. The microstructure of $\beta$-Ga$_2$O$_3$ nanomaterials was investigated by high-resolution transmission electron microscopy (HRTEM) and electron energy-loss spectroscopy (EELS). Results show that four major types of morphology were exhibited for these Ga$_2$O$_3$ nanowires during different proportions of catalysts, the particle-fused nanowires, single-crystal nanowires, nanorods and crystalline-amorphous core–shell nanowires were produced. Three $\beta$-Ga$_2$O$_3$ nanomaterials were studied in particular, single-crystal nanowires, particle-fused nanowires, crystalline-amorphous core–shell nanowires, respectively. EELS spectra analysis verified that the amorphous shell was Ga$_2$O$_3$. The growth behavior of $\beta$-Ga$_2$O$_3$ nanowires was discussed and a vapor-solid (VS) growth mechanism was proposed to explain the single crystal Ga$_2$O$_3$ nanowires.
2. Experimental

β-Ga2O3 nanowires were synthesized by a thermal CVD method and NiCl2 catalyst were prepared by a typical chemical process. The raw materials were metal Ga powder (Aladdin, purity: 99.9%), NiCl2·6H2O crystal (Aladdin, purity: 99.9%), CaF2 (Aladdin, purity: 99.5%), O2 (purity: 99.999%), N2 (purity: 99.999%) and Si (111) wafers. The samples were prepared in a high temperature diffusion furnace. A schematic of the CVD system used to grow gallium oxide nanowires is shown in figure 1.

The silicon (111) wafer substrate was cleaned in a NiCl2 solution with ethanol for 1 h, dried in air, and were placed on a quartz carrier. Then, metal gallium (Ga), calcium fluoride (CaF2, as a dispersing agent), and metal tin powder (Sn, as the doping source) was mixed according to the required proportions of the experiment 28, 29. The flow rate of O2 and N2 is the same (100 sccm). Firstly, N2 with flow rate of 100 sccm was used to drive the remaining air out and lasted for 5 min, and then the 30 min oxygen oxidation, finally ventilation the 10 min nitrogen to drive residual oxygen. The weight ratio of Ga/CaF2/Sn in the mixture is 1:2:0.02, and the mixture of Ga/CaF2/Sn and the Si substrate are in the same boat.

They were ground for 30 min to an agate mortar. When the furnace was heated to an equilibrium temperature of 1050 °C, flowing nitrogen was introduced into the tube for 5 min to flush the air. Next, the quartz boat with the Si (111) wafers and evaporated source powders was pushed into the constant thermal region of the furnace. Oxygen was added from the other side (time depending on the experimental conditions), then flushed with nitrogen for 10 min. Finally, the samples can be removed from the quartz boat. The volume percentage of NiCl2 is 1%, 2%, 4%, respectively.

The microstructure of the samples was investigated using a JEOL 2100 F transmission electron microscopy (TEM). EELS was performed on an FEI Tecnai F20 TEM. All the EELS spectra were acquired in image mode with a collection half-angle of ~16 m rad.

3. Results and discussion

3.1. Microstructure of β-Ga2O3 nanomaterials

Figure 2 displays the morphologies of the synthesized β-Ga2O3 nanomaterials which were measured by TEM. It is clear that the β-Ga2O3 nanomaterials have four different micro-morphologies: particle-fused nanowires, single-crystal nanowires, nanorods, and core–shell nanowires. Figure 2(a) shows the β-Ga2O3 nanowires formed by the fusion of particles. The β-Ga2O3 nanowires are composed of many Ga2O3 nanoparticles with a diameter of about 180 nm and are in an irregular arrangement. Figure 2(b) shows the TEM bright field image of a single crystal Ga2O3 nanowires. As seen in the figure, the surface of the nanowire is smooth, varies in length from tens of nanometers to several hundred nanometers, and the diameter of the nanowires is about 30 nm. In previous reports, the length of prepared Ga2O3 nanowires is generally several hundred nanometers, the diameter of the Ga2O3 nanowires is several tens of nanometers [30]. Figure 2(c) shows Ga2O3 nanorods. The surface of the nanorods is smooth. The length ranges from 300 nm to 1.3 μm and the diameter is about 150 nm. Figure 2(d) is a transmission electron microscopy picture of the β-Ga2O3 nanowires with a core–shell structure. It can be seen easily in the figure that the nanowires have a core–shell structure. The core is monocryrstalline Ga2O3, the shell is amorphous Ga2O3, the diameter of the nanowires is about 40 nm, and the thickness of the shell is about 30 nm shown by the follow-up high resolution TEM image and EELS analysis. The different microstructure of β-Ga2O3 nanomaterials is results from the different ratio of the catalyst. When the ratio of the catalyst is 1%, the nanowires are mainly composed of nanocrystals. When the ratio of the catalyst is 2%, the main product is single crystal nanowires which have partial core–shell nanowires. When the proportion of catalyst ratio is increased to 4%, the main products are nanorods and partial core–shell nanowires. The reasons for this phenomenon are as follows: when the proportion of catalysts is small, it is too small to play a role in guiding the growth of nanowires,
therefore, the main product is particle-fused nanowires. When the proportion of catalyst increases, single crystal nanowires and core–shell nanowires appear. NiCl$_2$ acts as catalyst and plays an important role in the growth of the $\beta$-Ga$_2$O$_3$ nanowires, because Ni$^{2+}$ is probably the nucleation point of the $\beta$-Ga$_2$O$_3$ embryos. The nanowires with core–shell structure were also obtained. This may be because the local distribution of the catalyst was not uniform, which resulted in the late crystallization of part Ga$_2$O$_3$, so the core–shell structure appeared.

3.2. TEM characterization and growth mechanism of $\beta$-Ga$_2$O$_3$ nanowires

Firstly, the characterization of monocrystalline $\beta$-Ga$_2$O$_3$ single crystal nanowires was studied. Figure 3 shows the scanning electron microscopy of Ga$_2$O$_3$ nanowires on the Si substrate. A large number of Ga$_2$O$_3$ nanowires were present on the Si substrate and were irregularly arranged. Figure 3(b) is a rectangular area of the enlarged picture. Careful observation reveals the surface of the nanowire is smooth and the thickness is relatively uniform. In addition, there is no orientation between the nanowires and the substrate, indicating that the nanowires are not epitaxially grown on the substrate. A more detailed crystal structure was revealed by HRTEM mode and SAED. The HRTEM images of Ga$_2$O$_3$ nanowires are displayed in figures 4(a) and (b). The clear lattice fringes confirm that the synthesized nanowires are single crystals. The closest interplanar distance is about 0.29 nm which corresponds the crystal (020) plane of $\beta$-Ga$_2$O$_3$. This indicates that the growth direction of the nanowire is [020]. Furthermore, the lattice is very perfect which indicates that the nanowire is a high-quality crystal lattice with no defects. The corresponding SAED pattern in figure 4(a) also reveals that the nanowire is monoclinic $\beta$-Ga$_2$O$_3$ and its growth direction is [020].

Figure 4(a) shows the HRTEM image of a single nanowire. Here, the nanowires are single crystal structures with a single nanowire diameter of about 40 nm and smooth. This is consistent with the results of scanning electron microscopy. The graphs in figure 4(a) are the constitutive electron diffraction patterns of nanowires according to the unit cell parameters of $\beta$-Ga$_2$O$_3$: $a = 4.98$ Å, $b = 4.98$ Å, $c = 13.43$ Å, $\alpha = \beta = 90^\circ$, and the calibration results are shown in the illustration. The diffraction spots are arranged in regular periods, and the
$\beta$-Ga$_2$O$_3$ is a single crystal structure. Figure 4(b) shows a high-resolution image of the rectangular area in figure 4(a). The crystal plane spacing of the resulting material is 2.91 Å, corresponding to a crystal plane (020) of $\beta$-Ga$_2$O$_3$ ($d(020)=2.82$ Å). In the monoclinic structure, the direction perpendicular to (020) is [202]. The growth direction of this nanowire is [202], as indicated by the black arrow in the figure.

Secondly, we further studied the growth mechanism of $\beta$-Ga$_2$O$_3$ single crystal nanowires. At present, the growth mechanism of one-dimensional nanomaterials mainly includes vapor-liquid-solid (VLS) [31, 32] vapor-solid-solid (VSS) [33] and vapor-solid (VS) [34] growth mechanism. It has reported that when use the catalyst, the growth would follow the VLS and VSS mechanism [26]. The classical characteristic of the VLS and VSS mechanism is that there is droplet observed at the top of the one-dimensional nanomaterials. In this experiment, NiCl$_2$ was used as catalyst, but no catalyst particles were found on the tip of the prepared Ga$_2$O$_3$ nanowire, so it was inferred that VLS and VSS mechanism was not suitable for our results. Unlike VLS and VSS methods, the VS method generally does not require the intervention of an external catalyst. Instead it uses the crystal itself to extend the growth rate of other crystals in different growth rates [35, 36]. Without catalyst, the growth of $\beta$-Ga$_2$O$_3$ nanowires would be categorized as VS mechanism, as suggested by other groups [37, 38]. Therefore, although we use the catalyst, the VS mechanism may be more suitable for the VLS one to demonstrate the growth of Ga$_2$O$_3$ nanomaterials.

It was inferred that Ni$^{2+}$ did not form an alloy with Ga during the growth of nanowire. During the heating process, gallium metal forms gaseous Ga atoms, which are transported by oxygen to the substrate covered by Ni$^{2+}$. The free gaseous Ga and O atoms are absorbed by Ni$^{2+}$ and then react to form nuclei. As the reaction progresses, the free Ga and O atoms continue to diffuse and grow along the preferred orientation, and finally Ga$_2$O$_3$ nanowire is obtained. Figure 5 shows the growth mechanism of Ga$_2$O$_3$ nanowires.
The chemical reaction equation for this experiment is as follows:

\[ 4\text{Ga} + 3\text{O}_2 \rightarrow 2\text{Ga}_2\text{O}_3 \]

As shown in figure 5, there is a layer of NiCl₂ catalyst on the Si substrate. During the reaction, the chemical bond of Ni-Cl in NiCl₂ breaks to produce Ni²⁺, which plays an important guiding role in the growth process of Ga₂O₃ nanomaterial [10, 38]. The catalytic mechanism is that Ni²⁺ can change the energy distribution of the substrate surface, that is to say, where there is a Ni²⁺ distribution, a large amount of defect energy will be generated, which leads to the growth of nanowires.

3.3. TEM study on particle fusion nanowires
When the other experimental conditions are constant and the catalyst ratio is 1%, the product is mainly pelletized nanowires. In the previous studies on Ga₂O₃ nanomaterials, few literatures have been studied the structure of particle fusion nanowires and core–shell nanowires by TEM. In this paper, the structure of particle fusion nanowires and core–shell nanowires was studied by SEM and TEM, respectively. The nanowires are not pure single crystals, but are composed of many grains, as shown in figure 6. Figure 6(a) is a scanning electron microscope (SEM) image of Ga₂O₃ nanowires on the substrate. The substrate formed a layer of dense Ga₂O₃ nanowires after the reaction. With careful observation, we can see the surface of the nanowires is not smooth. The nanowires are made of a pile of grains. In order to further observe the morphology of the Ga₂O₃ nanowires, the rectangular region in (a) was enlarged, as shown in figure 6(b). It can be seen from figure 6(b) the diameter of the nanowires is about 200 nm. Figure 6(c) shows a bright field of Ga₂O₃ nanowires using TEM, where the surface of the nanowires is rough and made up of many different grains. The diameter of the nanowires is about 180 nm. Additionally, there are some bright areas marked with the rectangular in figure 6(c) in the nanowires. In order to further study the exact structure of this bright area, HRTEM was applied. As shown in figure 6(d), the bright area marked in figure 6(c) is composed by two grains. The white dotted line in the figure 6(d) indicates the interface between the nanocrystals and the different grains. In addition, it can be observed that the lattice fringes of the lower grains are very clear and the lattice fringes of the upper grains are very blurred due to the different orientations of the grains. The plane spacing of two parallel white lines is 2.92 Å, which corresponds to the (004) plane of β-Ga₂O₃. Through the observation of TEM and SEM, two points can be obtained. First, dense Ga₂O₃ nanowires formed on the substrate, and the surface of the nanowires is rough with no fixed growth direction. Second, Ga₂O₃ nanowires are made of different grain piles, and there is no fixed orientation between the grains.

3.4. TEM study on β-Ga₂O₃ nanowires with core–shell structure
In the process of preparing β-Ga₂O₃ nanowires, we found that there was another form of β-Ga₂O₃ nanowires synthesized when the catalyst was increased to 2%, the core–shell structure of the β-Ga₂O₃ nanowires shown in figure 7. Figure 7(a) is a field TEM image of a single core–shell structure nanowires. It is clear that the nanowires have a core–shell structure, the diameter is about 60 nm, and the shell thickness is about 40 nm. Compared with monocrystalline nanowires, the core–shell nanowires have a relatively large diameter. The constitutive electron diffraction pattern, which can be seen from the diffraction point clear, is arranged neatly. Figure 7(b) shows the HRTEM image of the core–shell structure β-Ga₂O₃ nanowires. The core is single crystal, and the spacing between two parallel white lines is 5.71 Å. This corresponds to the (100) crystal plane (d₁₀₀ = 5.60 Å) of β-Ga₂O₃. The growth direction of the core–shell nanowires is [100], as shown by the black arrow in figure 7(a). This is different from the growth direction [202] of the single crystal nanowires studied earlier. The shell is an obviously amorphous. In order to confirm the specific composition of the core–shell, an EELS analysis was produced and is shown in figure 8.
Figure 8 shows the EELS spectrum were obtained from the amorphous shell on the surface of nanowire corresponding to figure 7(a). Figure 8(a) shows the EELS of O-K. The characteristic peak is about 536 eV, which corresponds to the O-K ionization loss peak, (b) is the EELS of Ga-L_{2,3}, with a peak at about 1222 eV, corresponding to Ga-L_{2,3}. This allows us to assume that the amorphous region has two elements, O and Ga, and the composition of the amorphous region is Ga_2O_3. Thus, the shell portion is uncrystallized Ga_2O_3.

Figure 6. (a) Typical scanning electron microscope image of the Ga_2O_3 nanowire; (b) The magnified image of the rectangular area in (a); (c) Typical TEM image of the Ga_2O_3 nanowire; (d) Typical HRTEM image for the nanowire. The ratio of NiCl_2 (catalyst) was 1%, β-Ga_2O_3 nanomaterials oxidized for 15 min.

Figure 7. (a) A low-magnified TEM image of β-Ga_2O_3 nanowires, The inset shows corresponding SAED pattern recorded along the [100]; (b) The enlarged HRTEM image of a white rectangular box marked in (a). The ratio of NiCl_2 (catalyst) was 2%, β-Ga_2O_3 nanomaterials oxidized for 15 min.
4. Conclusions

In summary, monoclinic $\beta$-Ga$_2$O$_3$ nanomaterials were successfully prepared by CVD method and were investigated by TEM. Four morphologies of $\beta$-Ga$_2$O$_3$ nanowires were obtained, grains stacked nanowires, single crystal nanowires and nanorods, core–shell structure nanowire, respectively. The results show that if the ratio of catalysts is different, morphology of $\beta$-Ga$_2$O$_3$ nanowires is different. When the ratio of catalyst is 1%, mostly stacked nanowires are obtained. When the proportion of catalyst is increased to 2%, single crystal nanowires are produced. When the catalyst ratio increased to 4%, nanorods are most common. The preferential growth orientation of the single crystal nanowires is $[202]$ and the growth mechanism of single crystal $\beta$-Ga$_2$O$_3$ was clarified by vapor-solid growth mechanism. The existence of Ni$^{2+}$ plays a very important role in the growth of Ga$_2$O$_3$ nanowires. It prompted Ga$_2$O$_3$ nucleation and encouraged the nanowire growth. Besides, the compositions of core–shell structure nanowire was studied, and the components of core and shell were all Ga$_2$O$_3$ which was confirmed by EELS.

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ORCID iDs

Lei Shang https://orcid.org/0000-0002-0036-204X

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