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Crystal growth of β-Ga_2O_3 by electric current heating method

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Abstract

Beta gallium oxide (β-Ga_2O_3) ceramic bars were heated by electric current under various ambient pressures. In atmospheric pressure, few crystals grew on the rod. In vacuum chamber (6.7×10^{-3} Pa), on the other hand, aggregated crystals were grown on the rod. The typical size of the aggregated crystal was approximately 50 μm. Whiskers of β-Ga_2O_3 were grown near the platinum electrodes and their diameter decreased with decreasing pressure. From the results, vacuum condition is considered to be an important factor for β-Ga_2O_3 crystal growth by electric current heating method.

Keywords: Gallium oxide; Electric current heating method; Crystal growth; Growth condition

1. Introduction

A material with deep ultraviolet emission is wanted to develop advanced optoelectronics devices such as high-density optical data storage. Beta gallium oxide is very attractive material for deep ultraviolet (UV) optoelectronics because of its wide band gap of approximately 4.8 eV [1]. This material is intrinsically insulator, and it exhibits the n-type conductivity originated from existence of oxygen vacancies [2]. In addition, β-Ga_2O_3 is chemically and thermally stable, which has been investigated as gas sensor for high temperature [3]. Cathodoluminescence is one of the practical techniques to investigate the defect and impurity level in semiconductors. Yu et al. [4] reported the cathodoluminescence of β-Ga_2O_3 nanoribbon/nanowire fabricated by catalytic growth.

Many groups reported the various synthesis methods for the past few years. The nano-structures of β-Ga_2O_3 were grown by catalytic growth [5–7], graphite/hydrogen reduction [8] and plasma reaction [9].

Nezaki et al. [10] discovered a novel crystal growth technique named "electric current heating method." ZnO crystals grown by this method have various crystal forms such as hollow prism, tetrapod-like crystal and whiskers. The obtained crystal exhibits the ultraviolet emission corresponding to the band gap of ZnO. The crystal growth by electric current heating method is related to vaporization of Zn and/or ZnO [10].

In the present work, we attempted to grow the crystal of β-Ga_2O_3 by electric current heating method, and the effect of ambient pressure on the growth was investigated.

2. Experiment

A powder of β-Ga_2O_3 (Kojundo Chemical Laboratory, 99.99% purity) was pressed into plate (20 mm × 20 mm × 5 mm) at 40 MPa and sintered at 1500 °C for 4 h in air. The relative density of the resultant sample was about 66%. The sample was cut into bars (approximately 15 mm × 1 mm × 1 mm). The outer edges of each bar were electroded using Pt paste. The distance between the electrodes was 10 mm. The bar was placed in a vacuum chamber (ULVAC, VPC-260) and the pressure was decreased to various pressures. A current flowed through the bar using a regulated dc power supply (Takasago Ltd., GP0110-1). In order to stabilize the generated heat from the ceramic bar, the current was controlled so that the electric power consumption was fixed at 18 W. Temperature of the sample surface was measured using an infrared-camera (NEC San-ei, TH3101MR). The morphology of the sample surface was observed using a scanning electron microscope (SEM; JEOL, JSM-5510). X-ray diffraction was measured using an X-ray

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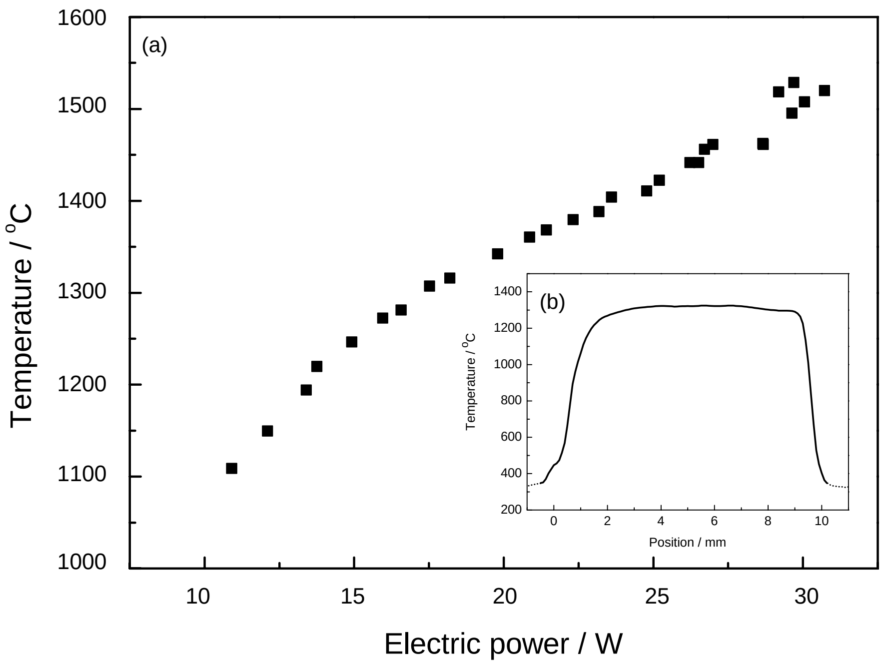

Fig. 1. (a) Relation between electric power and surface temperature of the β-Ga_2O_3 ceramic rod in air. (b) Temperature distribution of the rod heated by electric power of at 18 W in air.

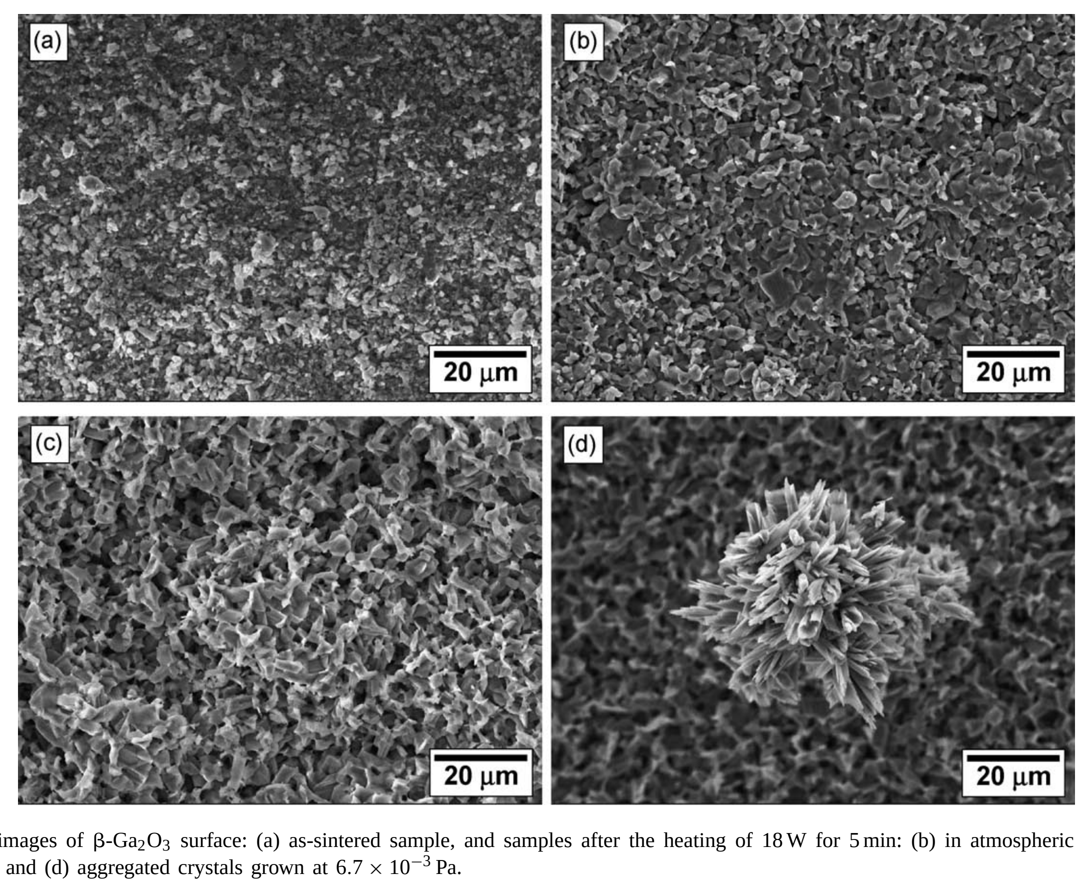

Fig. 2. SEM images of β-Ga_2O_3 surface: (a) as-sintered sample, and samples after the heating of 18 W for 5 min: (b) in atmospheric pressure, (c) at 6.7×10^{-1} Pa and (d) aggregated crystals grown at 6.7×10^{-3} Pa.

diffractometer (XRD; Rigaku, RAD-2C). Cathodoluminescence of the sample was measured using electron-beam accelerated by 5 kV at room temperature. The luminescence was collected using an ellipsoidal mirror and led into a monochromator (Jobin Yvon, TRIAX-320) through an optical quartz fiber. A grating (150 lines/mm) and a charge coupled device (CCD; Jobin Yvon, CCD1024x256-0) were employed in the monochromator for spectral detection.

3. Results and discussion

Fig. 1a shows the relation between electric power and surface temperature of middle part of the rod and Fig. 1b shows the temperature distribution of rod heated by electric power of 18 W in air. The surface temperature increased with increasing electric power. The rod was heated uniformly excepting in the area near the electrodes. The temperatures near the electrodes were lower than that of the rest of the rod because of heat dissipation caused by the electrodes. The temperatures measured in middle of the rod and nearby electrode were approximately 1300 and 1000 °C, respectively, when the power of 18 W was applied in air.

Fig. 2 shows SEM images of as-sintered sample (a) and samples after the heating of 18 W for 5 min: in atmospheric pressure (b), at 6.7×10^{-1} Pa (c) and at 6.7×10^{-3} Pa (d). The grain growth occurred and the ceramics became porous by the heating. The aggregated crystals were grown on the surface by the heating at 6.7×10^{-3} Pa. The typical size of aggregated crystals was approximately 50 μm. These results imply that the crystal growth of β-Ga_2O_3 was accelerated in the vacuum condition.

Nezaki et al. [10] reported that the vapor pressure of Zn was one of the important factors in crystal growth of ZnO by electric current heating. For ZnO crystal growth, the vapor pressure of Zn during the heating was approximately 1×10^5 Pa at 1000 °C, which is close to the atmospheric pressure. On the other hand, the vapor pressure of Ga is approximately 1×10^2 Pa at 1300 °C, which is expected during the heating of 18 W. Due to quite a low vapor pressure, the β-Ga_2O_3 crystals were hardly grown on the surface of ceramic bar heated at 18 W in atmospheric pressure.

Fig. 3 shows the SEM images of β-Ga_2O_3 whiskers grown on the bar nearby boundaries between ceramics and electrodes: in atmospheric pressure (a), at 6.7×10^{-1} Pa (b), and at 6.7×10^{-3} Pa (c). The temperature of the rod nearby the electrode was about 1000 °C during the heating. Some groups reported the catalytic growth of β-Ga_2O_3 nano-structures using metals such as Ni [5], In [6], Ag [7]. Though, the growth mechanism of obtained whiskers is under consideration, Pt used as electrodes might act as catalyst.

Fig. 4 shows the XRD pattern of as-sintered sample (a) and samples after the heating of 18 W for 5 min: in atmospheric pressure (b), at 6.7×10^{-1} Pa (c) and at 6.7×10^{-3} Pa (d). All the peaks were attributed to β-Ga_2O_3. The intensity

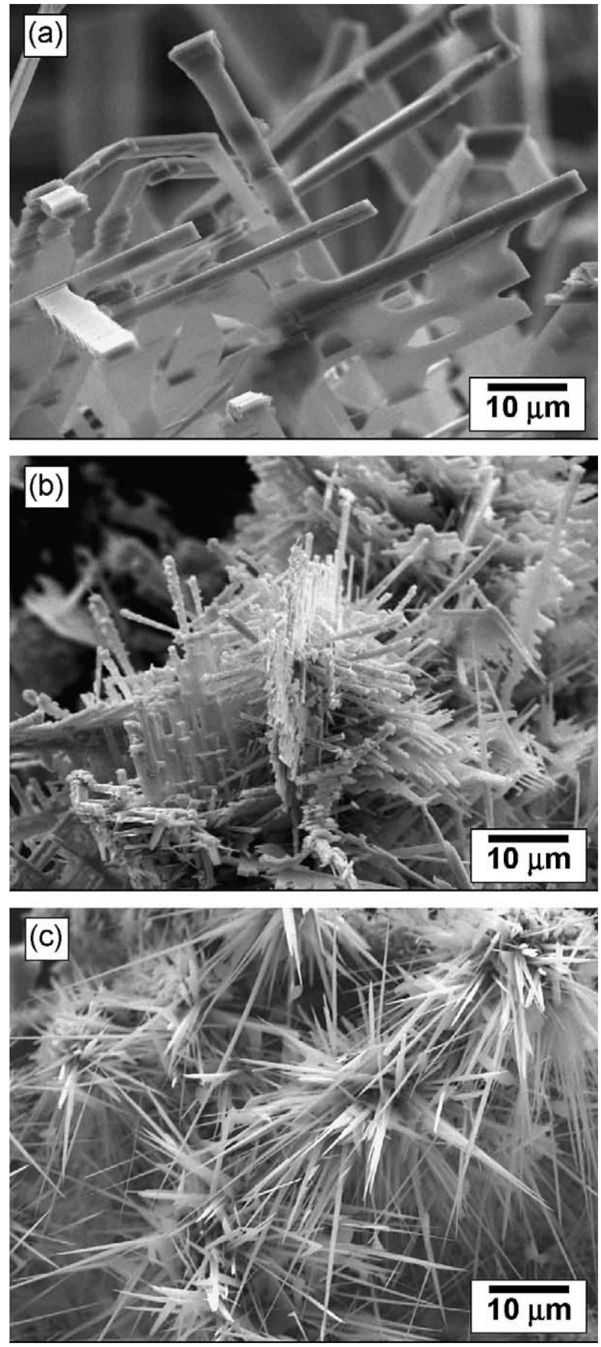

Fig. 3. SEM images of β-Ga_2O_3 whiskers grown nearby Pt electrodes after the electric current heating: (a) in atmospheric pressure, (b) at 6.7×10^{-1} Pa and (c) at 6.7×10^{-3} Pa.

ratio shown in Fig. 4d is different from those in Fig. 4a–c. This difference is considered to be caused by grown crystals with various orientations.

Fig. 5 shows cathodoluminescence spectra obtained from as-sintered sample (a), and samples after the heating of 18 W for 5 min: in atmospheric pressure (b), at 6.7×10^{-1} Pa (c), at 6.7×10^{-3} Pa (d) and aggregated crystals grown at 6.7×10^{-3} Pa (e). The deep ultraviolet emission from the band gap of β-Ga_2O_3 was not observed. All spectra showed

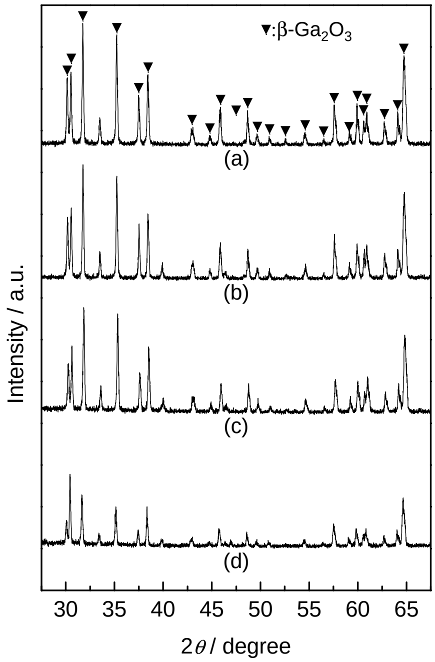

Fig. 4. XRD patterns of (a) as-sintered sample and samples after the heating of 18 W for 5 min: (b) in atmospheric pressure, (c) at 6.7×10^{-1} Pa and (d) at 6.7×10^{-3} Pa.

broad distributions from blue to ultraviolet with peak at 3.4 eV. The luminescence around 2.9 eV was increased in the sample heated under vacuum condition. However, in aggregated crystals grown at 6.7×10^{-3} Pa, the blue luminescence around 2.9 eV was not observed. This result might be explained in terms of the difference of defect structure. The aggregated crystals were grown from vapor phase, while grains in the ceramic bar were grown from solid phase.

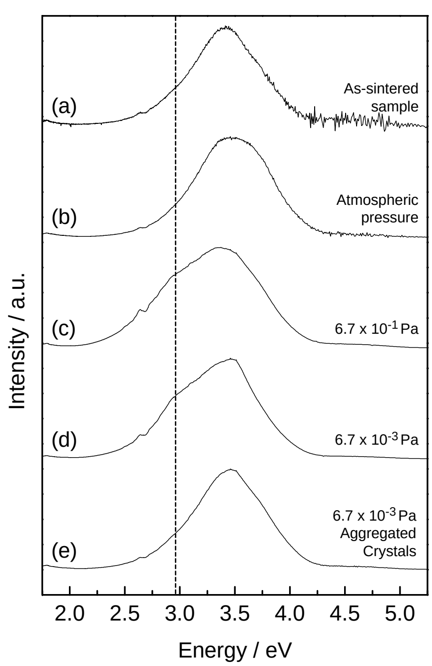

Fig. 5. Cathodoluminescence spectra of (a) sintered sample and samples after the heating of 18 W for 5 min: (b) in atmospheric pressure, (c) at 6.7×10^{-1} Pa, (d) at 6.7×10^{-3} Pa and (e) aggregated crystals grown at 6.7×10^{-3} Pa.

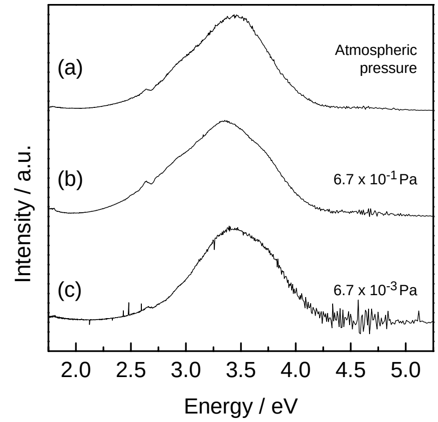

Fig. 6. Cathodoluminescence spectra of whisker grown nearby electrodes after the electric current heating: (a) in atmospheric pressure, (b) at 6.7×10^{-1} Pa and (c) at 6.7×10^{-3} Pa.

Fig. 6 shows cathodoluminescence spectrum obtained from β-Ga_2O_3 whiskers grown nearby electrodes (a) in atmospheric pressure, (b) at 6.7×10^{-1} Pa and (c) at 6.7×10^{-3} Pa. The spectra were similar to each other. This result suggests that the defect formation of the whiskers might not be related to ambient pressure in case of low temperature and/or catalytic growth.

4. Conclusion

Crystal growth of gallium oxide by electric current heating method was investigated under various ambient pressures. The aggregated crystals were grown on the ceramic surface at 6.7×10^{-3} Pa. The whiskers were grown nearby the Pt electrode in various ambient pressures. The results suggest that the vacuum is one of the most effective factors for the crystal growth of β-Ga_2O_3 by electric current heating method.

Acknowledgements

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