Extended Abstracts of the 2014 International Conference on Solid State Devices and Materials, Tsukuba, 2014, pp524-525

Synthesis of Gallium Nitride Nanostructure by Ammoniating the Electrochemically Deposited Gallium Oxide on Silicon Substrate

Norizzawati Mohd Ghazali[1], Mohamad Rusop Mahmood[2], Kanji Yasui[3], Abdul Manaf Hashim[1,*]

[1]Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Malaysia
*Email: abd_manaf@ic.utm.my
[2]Faculty of Electrical Engineering, Universiti Teknologi MARA, Malaysia
[3]Department of Electrical Engineering, Nagaoka University of Technology, Japan

Abstract

GaN nanostructures were successfully produced by the nitridation of the electrochemically deposited Ga_2O_3 through the utilization of a so-called an ammoniating process. Ga_2O_3 nanostructures were deposited on Si substrate by a simple two-terminal electrochemical technique at a constant current density of 0.15 A/cm^2 using a mixture of Ga_2O_3, HCl, NH_4OH and H_2O for two hours. After the ammoniating process, a prominent peak at 32.9° was observed and this peak corresponds to c-GaN(100). There is no diffraction peak of Ga_2O_3 observed after the ammoniating process which seems to indicate a complete nitridation of Ga_2O_3. The nitridation of Ga_2O_3 was achieved at relatively low temperature of 800 °C. These results show that the presented methods seem to be promising in producing high quality c-GaN nanostructures.

1. Introduction

Gallium nitride (GaN) is a direct wide band gap semiconductor with superb properties which makes it suitable to be used for high power optoelectronic devices such as light emitting diode (LED), transistor and sensor [1,2]. Up to this date, many techniques have been explored to synthesize GaN nanostructures including nanowires, nanorods, nanodots and so forth since such low dimensional structures are promising for huge astonishing applications [3,4]. For example, GaN nanorods have been applied for chemical sensing application as reported by Wright *et al*. due to large surface to volume ratio [5]. GaN nanodots have been used in photodetector as reported by Mahesh *et al.* [6].

Recently, GaN on silicon carbide (SiC) or sapphire substrate have been widely used for several electronic applications due to specific requirements. However, these substrates are expensive and not available in large wafer size [7]. According to Kukushkin *et al.* silicon substrate is believed to be more preferable due to the availability of large wafer size and low price [8]. In addition, the integration of GaN based devices on Si platform seems to be very attractive for the hybrid integration towards "More than Moore" technology. In this work, we investigate the formation of GaN nanostructures by ammoniating the electrochemically deposited beta gallium oxide (β-Ga_2O_3) on silicon substrate.

2. Experimental procedures

The synthesis involves two major processes; i) a formation of Ga_2O_3 structures as seeding structures, and ii) an ammoniating process to transform Ga_2O_3 to be GaN. The growth of Ga_2O_3 on silicon substrate was carried out by a two-terminal electrochemical process. In electrochemical process, a mixture of Ga_2O_3 (99.99 %), HCl (36 %), NH_4OH (25 %), and DI water was used as an electrolyte. Since Ga_2O_3 is insoluble in water, HCl is added to dissolve Ga_2O_3. The preparation of electrolyte was done as follows. First, Ga_2O_3 was dissolved in 1.5 ml HCl. Then, 6.5 ml DI water was added into the solution, followed by NH_4OH as a precipitator, so that the pH of the mixture could be easily adjusted. The growth was done in electrolyte with Ga_2O_3 molarity of 1.0 M at pH 6. The deposition was done at a constant current density of 0.15 A/cm^2. Si (100) with resistivity of 15 to 25 Ω·cm was used as the substrate. The substrate was cleaned with modified RCA cleaning using ethanol, acetone, and DI water prior to the deposition in order to remove a native oxide layer. The growth time was fixed at 2 h. In this electrochemical process, a platinum (Pt) wire was used as an anode and Si substrate as a cathode. After the deposition, the sample was dipped into the DI water to remove any unwanted residue. Recently, we reported the synthesis and properties of Ga_2O_3 formed on Si substrate by an electrochemical process [9].

The electrochemically deposited Ga_2O_3 was ammoniated in a vacuum chamber facilitated with heater. In this nitridation process, ammonia gas was used. The nitridation temperatures was set at 800°C and 850°C and the nitridation was done for 15 minutes under ammonia flow rate of 25 sccm (base pressure =100 Torr). Before starting the nitridation process, the sample was put inside the vacuum chamber. After the chamber is vacuumed for a few hours, the temperature of the substrate was raised to the desired temperature. Then, an ammonia gas was flown into the chamber for 15 minutes. After the ammoniating process, the remaining ammonia gas inside a chamber was flushed out with nitrogen gas. Finally, the sample is taken out from the chamber for the characterization. The nitridated structures were characterized using field-emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD).

3. Results and discussion

Fig. 1 shows the top view FESEM images of the electrochemically deposited Ga_2O_3 samples on Si substrate at

Ga_2O_3 molarity of 1.0 M with pH 6 before ammoniating process was applied. The FESEM image shows a mixture of Ga_2O_3 nanorods and nanodots on the Si substrate. The lengths of the grown Ga_2O_3 nanorods were estimated to be in the range of 1000 to 4200nm and the diameter in the range of 200 to 1000nm. While, the diameter of Ga_2O_3 nanodots were estimated to be in the range of 200 to 1000nm. The EDX spectra show that the grown structures contain Ga and O element, indicating the formation of Ga_2O_3 nanostructure. The details on the synthesis of Ga_2O_3 can be found in ref. [9].

Fig. 2 shows the XRD spectra of the same sample before and after the ammoniating process at temperature of 800°C and 850°C. Before the ammoniating process, three prominent peaks were observed at 30.5°, 31.8° and 33.1° which correspond to β-Ga_2O_3(40-1), β-Ga_2O_3(02-2) and β-Ga_2O_3(11-1), respectively. After the ammoniating process, a prominent peak at 32.9° was observed for both samples annealed at 800°C and 850°C and this peak corresponds to c-GaN(100). There is no diffraction peak of Ga_2O_3 observed after the ammoniating process which seems to indicate a complete nitridation of Ga_2O_3.

Based on the analysis, the transformation of Ga_2O_3 to GaN can be described as follows. Firstly, ammonia (NH_3) decomposes to NH_2, NH, H_2 and N at high temperature of 850°C as illustrated by eq.1 [10]. Then, Ga_2O_3 particles are deoxidized by H_2 to form gaseous Ga_2O as illustrated by eq.2. Finally, GaN structure is synthesized through the reaction of Ga_2O and NH_3.

$$2NH_3\,(g) \longrightarrow N_2\,(g) + 3H_2\,(g) \quad (1)$$

$$Ga_2O_3(s) + 2H_2(g) \longrightarrow Ga_2O(g) + 2H_2O\,(g) \quad (2)$$

$$Ga_2O(g) + 2NH_3(g) \longrightarrow 2GaN(s) + 2H_2(g) + H_2O(g) \quad (3)$$

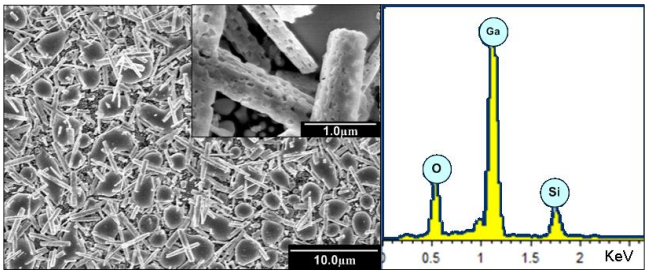

Fig. 1 Top view of FESEM image of electrochemically deposited Ga_2O_3 structures formed on Si substrate at Ga_2O_3 molarity of 1.0 M with pH 6.

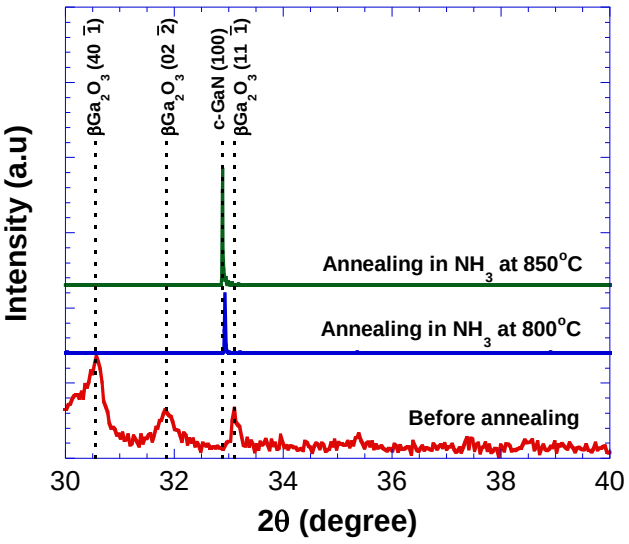

Fig. 2. XRD spectra of samples before and after the ammoniating process at different temperatures.

3. Conclusions

The electrochemically deposited Ga_2O_3 nanostructures were completely transformed to c-GaN by the ammoniating process at relatively low temperature of 800 °C. The results show that the presented methods seem to be promising in producing high quality c-GaN nanostructures.

Acknowledgements

N.M Ghazali thanks Malaysia-Japan International Institute of Technology for the scholarship. This work was funded by Nippon Sheet Glass Corp., Hitachi Foundation, Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Malaysia Ministry of Science, Technology and Innovation and Malaysia Ministry of Education.

References

[1] H.M. Kim et al., Adv. Mater. **15** (2003) 567.
[2] K. Toshihide et al., Fujitsu Sci. Tech. J **48** (2012) 40.
[3] S. K. Moon et al., Nano Energy **1** (2012) 39.
[4] M. S. Shur et al., Solid State Electron **42** (1998) 2131.
[5] J. S. Wright et al., Semicond. Sci. Technol. **25** (2010) 1.
[6] K. Mahesh et al., App. Phy. Express **5** (2012) 1.
[7] S. Pal et al., Bull. Mater. Sci. **27** (2004) 501.
[8] S. A. Kukushkin et al., Rev. Adv. Mater. Sci. **17** (2008) 1.
[9] N.M. Ghazali et al., Nanoscale Res. Lett. **9** (2014) 1.
[10] F. Shi et al., Mater. Sci. **663** (2011) 356.