Synthesis of beta gallium oxide nano-ribbons from gallium arsenide by plasma immersion ion implantation and rapid thermal annealing

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Received 27 October 2003; in final form 27 October 2003

Abstract

We report the synthesis of $\beta$-phase Ga$_2$O$_3$ nano-ribbons by plasma immersion ion implantation (PIII) and rapid thermal annealing (RTA). Undoped GaAs substrate was treated with PIII of nitrogen. RTA at 950 °C for 2 min produced clusters of single crystalline $\beta$-Ga$_2$O$_3$ nano-ribbons. These nano-ribbons have thickness of around 30 nm and widths 60 nm to 2 $\mu$m. The nano-ribbons start off directly from Ga$_2$O$_3$ grains on the surface and they emit blue light. Nano-wire growth usually involves a vapour–liquid–solid process in which metallic particles act as a condensation catalyst. However, we believe that the present case is likely to involve a vapour-solid mechanism.

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1. Introduction

Nano-sized materials possess unique electronic, optical and magnetic properties superior to traditional bulk materials due to their quantum size effects. They also serve as potential building blocks for high performance electronic and optoelectronic devices. Indeed quasi one-dimensional nano-sized materials, including GaAs, GaN, Ga$_2$O$_3$ and SiO$_2$ have been fabricated [1], and they have been used in high gain field effect transistors and low threshold lasers. Research into the synthesis and characterization of various forms of nano-sized materials has therefore become a very important research topic in recent years. As for gallium oxide, we know that $\beta$-Ga$_2$O$_3$ is a wide band gap ($E_g = 4.9$ eV) compound [2] and it has long been known to exhibit both conduction and luminescence properties [3]. Gallium oxide nano-wires should have potential applications in one-dimensional optoelectronic nano-devices. Until now several synthesis methods of crystalline gallium oxide nano-wires have been reported. They include arc discharge of GaN powder [4], evaporation of bulk Ga [1], or annealing of Ga$_2$O$_3$ powder with
carbon nano-tubes [5]. In this Letter, we report that gallium oxide nano-ribbons have been synthesized by plasma immersion ion implantation (PIII) [6] of nitrogen into GaAs and post-implant rapid thermal annealing. In addition, the growth mechanism of the gallium oxide nano-ribbons has been discussed.

2. Experimental

In the experiment, the GaAs sample was implanted by nitrogen ions under a pulsed mode. The PIII instrument is designed to deliver better than \( \pm 2\% \) uniformity across a 300 mm wafer. The chamber is made of aluminium and heating or cooling can be applied to the sample stage. Details of the design of the PIII equipment can be found elsewhere [6]. Before PIII of nitrogen, a 10 min cleaning step, using argon ions was performed at a bias voltage of 300 V. Afterwards, pulsed implantation of nitrogen was conducted with pulse duration \( t_p = 300 \, \mu s \) and a repetition rate of \( f = 200 \, Hz \). Within the implantation process, the GaAs sample was implanted under three different acceleration voltages: 40, 20 and 10 kV and the respective dosages, were \( 8 \times 10^{16}, 5 \times 10^{16} \) and \( 3 \times 10^{16} \, cm^{-2} \). Implantation temperature was kept below 300 \( ^\circ C \) to prevent activation of nitrogen in GaAs during implantation. The use of multiple energy values ensured a relatively broad distribution of nitrogen and more effective area amorphization. The depth profile was simulated by TRIM [7], which indicated that a highly saturated nitrogen-doped GaAs layer was formed within 400 \( \AA \) from the surface.

After the PIII process, rapid thermal annealing (RTA) was performed on the GaAs sample. Five samples were annealed at 800, 850, 900, 950 and 1000 \( ^\circ C \), respectively. All samples were annealed for 2 min without any surface protection. 99.9% nitrogen gas was flowing inside the rapid thermal annealing chamber at a rate 3 l/min. For the samples annealed at 900 \( ^\circ C \) or above, a white coloured thin film was found on the sample surface. This white coloured material was characterized using a field emission scanning electron microscope (FE-SEM), Jeol SEM 820, operating at 5 kV, and a transmission electron microscope (TEM), Philips TEM CM20, operating at 200 kV. XPS measurements were conducted using a Physical electronics PHI 5600. A Renishaw Micro-Raman RM3000 was used to perform Raman spectroscopy on the material. In addition, photoluminescence (PL) was also conducted to study the luminescence properties of the material. The PL measurements were carried out at room temperature using a He–Cd laser (wavelength: 325 nm, power: 5 mW) as the excitation source.

3. Results and discussion

First we conducted XPS on the PIII treated samples before RTA. The atomic concentration of gallium, arsenic, nitrogen, oxygen and carbon at the depth of 5 nm were found to be 49%, 26%, 15%, 10% and 0%, respectively. Although we only implanted nitrogen into the GaAs sample, our result showed that a relatively high level of oxygen was also incorporated into the sample. Moreover, the oxygen concentration decreased rapidly to 1% within the depth of 15 nm. We believe, that the high level of oxygen came from the residual oxygen trapped in the aluminium implantation chamber wall.

Fig. 1a shows a SEM image of the white coloured material found on the sample which went through RTA at 950 \( ^\circ C \) for 2 min. Randomly oriented nano-ribbons with widths ranging from 60 nm to 2 \( \mu m \) and thickness of approximately 30 nm are observed. The lengths are up to tens of microns. Electron X-ray dispersive analysis was performed on a cluster of the nano-ribbons and the corresponding spectrum is shown in Fig. 1b. Strong peaks of gallium and oxygen are found, indicating the formation of gallium oxide. Fig. 1c shows Raman spectrum of the nano-ribbons. The narrow Raman peaks found at 197, 318, 342, 413, 473, 629 and 652 cm\(^{-1}\), match exactly to those observed from single crystal of \( \beta-Ga_2O_3 \) [4,8].

In Fig. 2, we show the room temperature PL spectrum of the nano-ribbons. Two strong peaks are seen at 418 and 439 nm. Binet et al. [9] performed PL characterization on a bulk Ga_2O_3 single crystal and found a peak at 435 nm. We therefore
believe that our PL peak at 439 nm suggests the formation of Ga$_2$O$_3$ single crystal. This peak is not due to interband transition, and in fact it comes from the recombination of bound electron-hole exciton in $\beta$-Ga$_2$O$_3$ single crystal. For the other peak at 418 nm, we believe that the quantum size effect associated with the nano-ribbon may cause a PL blue-shift to a shorter wavelength.

In order to understand the mechanism leading to the formation of the nano-ribbons, we first take a look at the models which have been widely accepted as the growth mechanisms for nano-sized and related materials. The first one requires the existence of a screw dislocation whose line is parallel to the axis of the ribbon [1]. In this model, the spiral plane perpendicular to the dislocation line provides a growth step, which serves as a low energy site, so that the axial growth rate is much faster than along radial direction. The second growth model involves the participation of eutectic alloys exiting at the tip of nano-wires. The so-called vapour–liquid–solid (VLS) growth [10,11] mechanism takes into account the fact that nano-wires grow much faster in the longitudinal direction via material condensation induced by the eutectic. The third model, which is called catalytic growth [2,12], is similar to the VLS process. The tip contains a small amount of transition metal, such as Au, Fe or Al, which performs a rapid catalytic growth of material along the longitudinal direction. Nano-wires produced by the VLS and catalytic techniques normally have a nano-particle attached to the tip of the wire.

In Fig. 3a, a TEM image of our nano-ribbon is shown. No screw dislocations are observed in the TEM image. Therefore it is unlikely for the nano-ribbons to be synthesized by a dislocation mechanism. On the other hand, Fig. 3b obtained by SEM also reveals that the free ends of the ribbons are free from any particles. This indicates that both the catalysis and VLS mechanisms may not be appropriate for explaining the growth process involved in our experiment.
The growth of our nano-ribbons may be explained on the basis of a vapour–solid (VS) mechanism. Wu et al. [3] performed synthesis experiments similar to those reported here. They annealed a mixture between Ga$_2$O$_3$ powder and carbon in argon and found Ga$_2$O$_3$ nano-wires deposited on the furnace wall surrounding the source holder. They did not observe liquid droplets at the wire ends. They proposed that the wires were grown via a VS mechanism. During annealing, Ga$_2$O$_3$ powder underwent a reduction reaction to produce Ga$_2$O and Ga vapour. After that, the Ga vapour oxidized in limited oxygen supply and deposited directly on the furnace surface to form Ga$_2$O$_3$ nano-wires. Their VS mechanism proposed for the growth of Ga$_2$O$_3$ nano-wires was also supported by Gundiah et al. [5]. They also found that the normal of growth planes makes a small angle of 6° with the growth direction, which indicated that Ga$_2$O$_3$ nano-wires can only grow along a particular growth plane. Peng et al. [13] studied the growth of GaN nano-wires and concluded that the nano-wires were grown via VS mechanism. They observed that a lower growth temperature favoured the growth of GaN nano-wires along some preferred crystal directions. Nevertheless, until now there is limited experimental data to provide a clear explanation on the growth mechanism of Ga$_2$O$_3$ nano-wires or nano-ribbons. Given the facts that we did not see the presence of any nanoparticles at the tips of the nano-ribbons and we used a high annealing temperature in excess of 950 °C, which would be adequate to produce much Ga vapour from the GaAs sample, we believe that our observation of Ga$_2$O$_3$ nano-ribbons was very likely to be produced via a VS mechanism.

One point we should mention is that in our Ga$_2$O$_3$ nano-ribbon synthesis experiments, the PIII of nitrogen into GaAs was an important step. We annealed a non-implanted GaAs under the same conditions but we did not observe any nano-ribbon on the sample. In other words, the necessary conditions were firstly the amorphization of the surface caused by ion implantation, and secondly a very limited supply of oxygen, which was only incorporated during the PIII step. Further studies are now on-going in order to identify the inter-play between PIII parameters and the annealing conditions.

4. Conclusions

In summary, we have described a method to synthesize β-phase Ga$_2$O$_3$ nano-ribbons by PIII of nitrogen and using GaAs as the starting material. The synthesized β-Ga$_2$O$_3$ nano-ribbons have widths ranging from 60 nm to 2 μm and lengths up to tens of microns. The strong PL peak at 418 nm shows that the β-Ga$_2$O$_3$ nano-ribbons may possess optical properties with possible applications in optoelectronic nano-devices. Although further data might be necessary in order to provide conclusive identification of the growth mechanism of the Ga$_2$O$_3$ nano-ribbons, we believe that our Ga$_2$O$_3$
nano-ribbons were most likely produced via a vapour–solid growth process.

Acknowledgements

The authors wish to acknowledge the support from a RGC CERG City U grant (project # 1052/02E) and the technical support from the Solid State Lab. at the CUHK. The research Studentship for K.C. Lo is also acknowledged.

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