Preparation of GaN thin film and Ga$_2$O$_3$ nanoribbons by plasma immersion ion implantation of N into GaAs

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A method for producing gallium nitride (GaN) and gallium oxide (Ga$_2$O$_3$) nanoribbons by the combination of plasma immersion ion implantation of nitrogen into GaAs and rapid thermal annealing (RTA) has been investigated. Our approach uses a broad ion-impact energy distribution with variable implant doses to form a spread-out nitrogen depth profile and an amorphous surface layer. This approach circumvents the retained-dose limitation and low nitrogen content problems associated with ion beam implantation at fixed energy. Raman spectroscopy, transmission electron microscopy (TEM), x-ray diffraction and x-ray photoelectron spectroscopy were conducted on the samples. For the samples which had undergone RTA at 850 °C for 2 min, a Raman peak at 577 cm$^{-1}$ associated with GaN was observed. The weak Raman intensity indicated that a small amount of GaN was present. Cross-sectional TEM imaging showed that the thickness of the region containing GaN was about 40 nm. When RTA was performed at 950 °C for 2 min, Ga$_2$O$_3$ nanoribbons were found on the GaAs sample surface instead. The ribbons were 0.1–2 μm in width, several tens of nanometers in thickness, and several tens of micrometers in length. Raman spectroscopy confirmed that the ribbons are single crystalline Ga$_2$O$_3$. In addition, the Ga$_2$O$_3$ ribbons were found to possess strong visible photoluminescence. The possible formation mechanism of these nanoribbons is discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1715137]

I. INTRODUCTION

The epitaxy of high-quality GaN and related compounds has spurred intensive research activities aimed at exploiting the potential of III-V nitrides as light emitting devices active in the full range of the light spectrum and as electronic devices suitable for high temperature, high power, and high frequency applications. Currently, many techniques including reactive sputtering, chemical vapor deposition, reactive molecular beam epitaxy, and their variations have been used to grow GaN thin films on a variety of substrates such as sapphire and SiC. Recently, several publications have already reported the successful synthesis of GaN on GaAs substrates via the nitrogen ion implantation route.\textsuperscript{1–7} Lin et al.\textsuperscript{3} showed that in GaAs the heavily nitrogen ion implanted surface contained nanosize crystals of cubic and hexagonal GaN after annealing at 850 °C. Kuriyama et al.\textsuperscript{4} also recently demonstrated that nitrogen ion implanted GaAs exhibits photoluminescence in the blue region. It shows the prospect of producing functional GaN by ion implantation. Another research group led by Yu\textsuperscript{8} prepared Ga$_x$As$_{1-x}$ thin films by nitrogen ion implantation. They also synthesized diluted InN$_x$P$_{1-x}$ and Al$_x$Ga$_{1-x}$N$_{1-y}$As$_y$ alloys by nitrogen implantation into InP and AlGaAs. They demonstrated that ion implantation could produce not only GaN films, but also other III-V materials. Moreover, all the above studies employ conventional ion beam implantation at fixed ion energy.

On the other hand, monoclinic $\beta$-phase gallium oxide ($\beta$-Ga$_2$O$_3$), which is a wide band-gap semiconductor with a band-gap energy of 4.9 eV, exhibits conduction and luminescence properties, and thus has potential applications in optoelectronic devices and gas sensors. In addition, gallium oxide nanowires may be suitable for making one-dimensional optoelectronic nanodevices. Until now several synthesis methods of crystalline gallium oxide nanowires have been reported. They include arc discharge of GaN powder,\textsuperscript{9} evaporation of bulk Ga,\textsuperscript{10} and annealing of Ga$_2$O$_3$ powder with carbon nanotubes.\textsuperscript{11}

In this paper the synthesis of GaN films and Ga$_2$O$_3$ nanoribbons by plasma immersion ion implantation (PIII) of nitrogen and postimplant rapid thermal annealing (RTA) are studied. We employ PIII in our implantation process because it can compensate the uniformity problem in conventional ion beam implantation and it can conveniently introduce a broad depth profile by multienergy implantation. The use of PIII and RTA to synthesize GaN films and Ga$_2$O$_3$ nanoribbons has not been reported elsewhere.

II. EXPERIMENTAL DETAILS

In the experiment, a GaAs wafer was implanted by nitrogen ions under a pulsed mode. Before nitrogen PIII, argon
cleaning was performed with a biased voltage of 300 V for 10 min. Subsequently, the pulse implantation was conducted for nitrogen ion PIII with a repetition rate of $f = 200$ Hz and pulse duration $t_p = 300 \mu$s. The GaAs sample was biased at three different voltages of 40 kV for 50 min, 20 kV for 25 min, and 10 kV for 15 min with implant doses of $8 \times 10^{16}$, $5 \times 10^{16}$, and $3 \times 10^{16}$ cm$^{-2}$, respectively. The implantation temperature was controlled below 300 °C for preventing nitrogen activation in GaAs during implantation. The use of multiple energy values ensures a relatively broad distribution of nitrogen and more effective area amorphization. After implantation, a highly saturated nitrogen-doped GaAs layer was formed within 400 Å of the surface, as shown in Fig. 1. The depth profile was simulated by TRIM.$^{12}$ This simulation shows that the peak nitrogen concentration is higher than the As concentration in the implanted GaAs.

Since ion implantation introduces severe damage to the wafer and the subsequent electrical conduction is dominated by deep-level traps, the resistivity is usually high. Annealing is needed to repair lattice damage and drive dopant atoms to substitutional sites. We applied RTA to the nitrogen implanted GaAs wafers. The implanted samples were annealed at 800, 850, 900, 950, and 1000 °C respectively. All samples were annealed for 2 min without any surface protection. The Raman spectra of the GaAs substrate before PIII were also studied by x-ray diffraction (XRD) with a Philips X'Pert x-ray diffractometer. In addition, photoluminescence (PL) and cathodoluminescence (CL) were also conducted to study the luminescence properties of the material. The PL measurements were carried out at room temperature and low temperature with 11 K using a He-Cd laser (wavelength: 325 nm, power: 5 mW) as the excitation source. For CL measurement, the sample was analyzed by an Oxford Instruments MonoCL system fitted to a scanning electron microscope. Finally, transmission electron microscopic (TEM) images were obtained using a Philips TEM CM20 operating at an accelerating voltage of 200 kV.

### III. EXPERIMENTAL RESULTS

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 results 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 aluminum implantation chamber wall.

#### A. Scanning electron microscopy (SEM)

For samples annealed at 800 and 850 °C for 2 min, we found a flat layer of a blue colored thin film on the GaAs surface. Moreover, some of the implanted samples were annealed at 900, 950, and 1000 °C for 2 min. For the samples annealed at 900 °C or above, white colored materials were found on the sample surface. Since no oxygen is present in the implanted GaAs, we only implanted nitrogen into the GaAs sample,

### B. Raman spectroscopy

The Raman spectra of the GaAs substrate before PIII and after PIII are shown in Figs. 3(a) and 3(b), respectively. In Fig. 3(a), the GaAs-type peaks at 268 cm$^{-1}$ (TO$_1$) and 292 cm$^{-1}$ (LO$_1$) are clearly seen.$^{13}$ The relative intensity of TO$_1$ is greater than that of LO$_1$, revealing that the GaAs substrate has been disordered and has many dislocations. The Raman spectrum of the implanted GaAs is shown in Fig. 3(b). A very broad peak at 232 cm$^{-1}$ with full width half at maximum of 100 cm$^{-1}$ is observed. The high background
intensity indicates that the surface layer is severely damaged after PIII implantation and an amorphous surface layer is formed.

Figure 4 shows the Raman spectra of the annealed samples at 800–1000 °C for 2 min. The excitation laser was focused on the blue colored area. At the spectrum of 850 °C, we can see that the GaAs-type peak at 268 cm\(^{-1}\) (TO\(_1\)) is clearly present. It indicates that the GaAs was recrystallized after annealing. After recrystallization of the nitrogen-implanted surface layer by RTA, many nitrogen atoms are inserted into substitutional lattice sites, and the surface layer

![FIG. 2. White colored material (nanoribbons) on sample RTA at (a) 900 °C, (b) 950 °C (Inset: high nanoribbon concentration area on sample edge), and (c) 1000 °C for 2 min.](image)

![FIG. 3. Raman spectra of GaAs sample; (a) before PIII, and (b) after PIII.](image)

![FIG. 4. Raman spectra of GaAs substrate after PIII and RTA at 800, 850, 900, 950, and 1000 °C for 2 min. (Inset: Raman spectra of Ga\(_2\)O\(_3\) nanoribbons of annealed samples at 900, 950, and 1000 °C.)](image)
is strained. In addition, a small GaN related peak at about 577 cm$^{-1}$ is observed in the spectrum. This is attributed to be a slightly red shifted peak (from a typical peak value of 568 cm$^{-1}$) which is believed to be associated with a compressively strained GaN thin film.$^{14}$ For the sample annealed at 800 °C. The GaN related peak and the TO$_1$ GaAs peak are almost absent. This suggests that the annealing temperature of 800 °C is not high enough to recrystallize the implanted surface. For the sample annealed at 850 °C, the GaN related peak is also weak but quite sharp. The weak Raman intensity revealed that only a small amount of GaN, possibly in small crystal form, is present. It appears that under the conditions adopted in our experiments, the implanted nitrogen atoms do not replace all the As atoms. The surface layer remains essentially a GaAs-type structure, and the nitrogen atoms have generated a strained GaAs layer in the surface. For the samples annealed above 900 °C, the GaN peak becomes even weaker. Moreover, new peaks at 198, 344, and 413 cm$^{-1}$ were found in all Raman spectra. They match exactly to those of single crystal of $\beta$-Ga$_2$O$_3$. $^{9,15}$ The spectrum of the sample annealed at 900 °C shows two GaAs Raman peaks, whereas no GaAs peaks are observed from sample annealed at 1000 °C. This may be due to the fact that a thick Ga$_2$O$_3$ film was formed under RTA at 1000 °C. So, the GaAs substrate could not be exposed and characterized by Raman spectroscopy.

**C. X-ray diffraction (XRD)**

XRD was conducted on the samples annealed at 800, 850, and 950 °C. For the sample annealed at 800 °C, the weak GaN peaks in the $2\theta$ scan are seen at 32.8° and 34.8° (see Fig. 4). The weak signal peaks indicate the presence of GaN, but the material quality is not very good. Figure 4 also shows the XRD spectrum of the sample annealed at 850 °C. The $2\theta$ peaks at 32.8°, 34.8°, and 37.1° are associated with hexagonal wurtzite GaN.$^{16}$ We also observed that the x-ray signals obtained from samples that were annealed at 800 °C are weaker than those coming from samples annealed at 850 °C. This may be attributed to the fact that recrystallization of the implanted layer is not complete at 800 °C. In addition, it also shows the XRD pattern obtained from the sample annealed at 950 °C. The peak positions may be indexed by those of monoclinic gallium oxide. Moreover, the relative intensities of the peaks are quite different from those of bulk Ga$_2$O$_3$, thus indicating the formation of nanosized materials. Strong peaks from the [4 0 0] and [1 1 1] planes are indicative of the formation of a $\beta$-Ga$_2$O$_3$ thin film on the sample surface, while the peak from the [0 0 2] plane points to the formation of $\beta$-Ga$_2$O$_3$ nanoribbons.$^{10,17}$ The lattice parameters of the $\beta$-phase Ga$_2$O$_3$ are $a = 12.227$ Å, $b = 3.0389$ Å, $c = 5.8079$ Å, $\beta = 103.82°$, and space group C$2/m$ (JCPDS 41-1103 database). Both Raman and XRD analyses confirm that the Ga$_2$O$_3$ are in the $\beta$ phase and of good crystal quality.

**D. Photoluminescence (PL) and cathodoluminescence (CL)**

We also conducted PL measurements for all annealed samples. The excitation source was focused on the flat surface where no Ga$_2$O$_3$ nanoribbon was seen. Figure 5 shows the PL spectra of the annealed samples. When the sample was annealed at 1000 °C, two broad emissions peaks at 570 and 700 nm are present. The width of the emission peak decreases with RTA temperature. The broad PL peaks are in the green and red spectral regions. It is not likely that they are related with dilute GaN materials. We believe that when the annealing temperature increases, the oxidation reaction of gallium metal becomes more active. These emissions may be due to defects in Ga$_2$O$_3$. Moreover, we found a lot of Ga$_2$O$_3$ nanoribbon clusters on the edge of the sample, and we measured their luminescence properties. In the inset of Fig. 6, we show the room temperature and 11 K PL spectra.

![FIG. 6. PL spectra of annealed samples. [Inset: room temperature (RT) and 11 K PL spectra of the nanoribbons formed under RTA at 950 °C.]](image-url)
of the nanoribbons formed under RTA at 950 °C. At room temperature, two strong peaks at 419 and 442 nm are observed. The peak at 442 nm comes from Ga₂O₃ film found on the GaAs surface after annealing. For the other peak at 419 nm, we believe that the quantum size effect associated with the nanoribbon may cause a PL blue shift to a shorter wavelength. At 11 K, the two peaks of β-Ga₂O₃ have blue shifted to 414 and 434 nm. Low temperature PL measurements on β-Ga₂O₃ have been reported by several groups. Binet and Gourier reported results similar to those obtained here, but their material was bulk Ga₂O₃ in the form of films. They measured the luminescence of a Zr-doped Ga₂O₃ film, and found that when the temperature was raised from 13 to 280 K, the intensity of the blue emission decreased. In the present case, the intensity of blue emission of our nanoribbons at 300 K is about 20% that at 11 K. In comparison to the results obtained by Binet and Gourier, the decrease of PL intensity of our nanoribbon is less than that of bulk Ga₂O₃ films. This result indicates that thermal quenching of PL is less significant in Ga₂O₃ nanoribbons. This is also generally true for systems with quantum confinement in which the density of states has steplike characteristics. The thick nanoribbons are rich in oxygen vacancies. We attribute this to the fact that the thin (produced at 950 °C) and thick (produced at 1000 °C) nanoribbons may have different distribution of defects, with different emission properties. On the other hand, the other broad peaks from 500 to 750 nm may be due to other defects deep in the band gap of Ga₂O₃. We believe that annealing at high temperature favors the oxidation reaction of metallic gallium to form Ga₂O₃. The emission observed in CL is primarily related to the energy position of the defect levels within the band gap of the Ga₂O₃ film.

![FIG. 7. CL spectra of the Ga₂O₃ nanoribbons on samples RTA at 950 and 1000 °C. (Inset: image of area selected for CL measurement. Upper image from sample RTA at 950 °C and lower from sample RTA at 1000 °C.)](image-7.png)

![FIG. 8. TEM image of nitrogen-implanted GaAs after RTA 850 °C.](image-8.png)

**E. Transmission electron microscopy (TEM)**

In Fig. 8, we show a cross-sectional TEM image of a sample annealed at 850 °C. From this TEM micrograph, we can see that the thickness of the nitrogen-implanted layer is about 40 nm. Moreover, EDAX indicates that the surface contains 15% oxygen. Some gallium oxide might have formed on the sample surface. In addition, our TEM micrograph reveals that voids with an average size of about 80–100 nm are present in the implanted layer. Yu et al. prepared GaNAs alloys by nitrogen ion implanted into GaAs. They also observed that similar small voids in the implanted layer. They suggested that these voids are nitrogen bubbles formed by segregation of nitrogen during annealing. Presence of these voids may suggest that only part of the implanted nitrogen atom would bind with gallium during annealing.

Figure 9 shows a TEM image of our nanoribbon which had been RTA at 950 °C for 2 min. It gives a very clear
electron diffraction pattern as well as no dislocations are observed. It means that the nanoribbons are of high crystal quality.

F. Formation mechanism of Ga$_2$O$_3$ nanoribbon

In Fig. 9, no screw dislocations are observed in the TEM image. Therefore it is unlikely for the nanoribbons to be synthesized by a dislocation mechanism. On the other hand, Fig. 2 obtained by SEM also reveals that the free ends of the ribbons are free from any particles. This indicates that both the catalysis and conventional VLS mechanisms may not be appropriate for explaining the growth process involved in our experiment. We therefore believe that the growth of our nanoribbons may be explained on the basis of a vapor-solid (VS) mechanism. In fact, Wu et al. 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$_3$ nanowires 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 vapor. After that, the Ga vapor oxidized in limited oxygen supply and deposited directly on the furnace surface to form Ga$_2$O$_3$ nanowires. Their VS mechanism proposed for the growth of Ga$_2$O$_3$ nanowires is also supported by Gundiah, Govindaraj, and Rao. Peng et al., who studied the growth of GaN nanowires. Their conclusion is that such nanowires are grown via a VS mechanism. They observed that a lower growth temperature favored the growth of GaN nanowires along some preferred crystal directions. The facts that we did not observe the presence of any nanoparticle at the tip of the nanoribbons and also that we used a high annealing temperature in excess of 950 °C, which would be adequate to produce much Ga vapor from the GaAs sample, strongly suggests that our observation of Ga$_2$O$_3$ nanoribbons is very likely to be produced via a VS mechanism.

One point we wish to mention is that in our Ga$_2$O$_3$ nanoribbon synthesis experiments, the PIII of nitrogen into GaAs was an important step. In the control experiments, we annealed a nonimplanted GaAs under the same conditions, but we did not observe any nanoribbon on the sample. On the other hand, the samples that went through PIII of argon and postimplant RTA at 950°C or above in nitrogen also did not give any nanoribbon. In other words, the necessary conditions must be: first, the amorphization of the surface caused by ion implantation; second, the reaction promoting action of implanted nitrogen; third, a very limited supply of oxygen, which is only incorporated during the PIII step. Further studies are now ongoing to identify the interplay between PIII parameters and the annealing conditions.

IV. CONCLUSIONS

In this paper we have demonstrated that PIII of nitrogen can generate GaN thin film and Ga$_2$O$_3$ nanoribbons. Raman and XRD studies revealed the presence of strained GaN after annealing at 850°C. The formation of GaN agrees with that reported in the literature. However, all previous experiments employed conventional ion beam implantation. The use of PIII and RTA to synthesize a GaN film on GaAs has not been reported elsewhere. The GaN material produced in the present case might be of low quantity and in nanosized crystalline form. Although the material quality of such GaN crystal might not be good enough for practical devices, we believe that further optimization might improve it and lead to the possibility of using such materials as a bridging layer for growing GaN on GaAs. After annealing at 950°C or above, Ga$_2$O$_3$ nanoribbons were found on the sample surface. This is a new material synthesis route for B-Ga$_2$O$_3$ as far as we know. A range of characterization techniques, including SEM, TEM, Raman, PL, and CL were performed on the nanoribbons. They revealed that our nano-ribbons are of high crystal quality. In addition, PL emission in blue light from the Ga$_2$O$_3$ nanosize materials may lead to device applications.

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