Formation of $\beta$-Be$_3$N$_2$ nanocrystallites in Be-implanted GaN

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Abstract

A small Be ion dose of $5 \times 10^{14}$ cm$^{-2}$ was implanted in a 2 $\mu$m thick GaN epilayer at an energy of 50 keV. The sample was characterized by high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy techniques after a post-implantation rapid thermal annealing (RTA) treatment. The HRTEM images show the crystallographic (1 1 0) and (0 0 2) planes of $\beta$-Be$_3$N$_2$. Two characteristic parallelograms drawn in Fast Fourier transform (FFT) image support the formation of $\beta$-Be$_3$N$_2$ nanocrystallites in RTA treated sample. Two Raman peaks at 168 and 199 cm$^{-1}$ are observed in the Raman spectrum of the sample that are assigned to $\beta$-Be$_3$N$_2$ on the basis of group theory and HRTEM data. The Raman peak at 168 cm$^{-1}$ is found close to the K point in the first Brillouin zone of $\beta$-Be$_3$N$_2$ while the peak at 199 cm$^{-1}$ is assigned as a combination mode of the fundamental Raman modes of $\beta$-Be$_3$N$_2$.

1. Introduction

Through the decades, GaN has been a subject of extensive research for its being one of the most promising wide band gap semiconductor materials for the fabrication of light-emitting diodes and injection lasers in the blue and ultraviolet spectral region, and of high power and high frequency devices [1–7]. Ion implantation is an effective method that allows the introduction of a precisely controlled dosage of impurity ions into the crystal. It plays a critical role in the realization of high-performance electronic and photonic devices in all semiconductor material systems [8–10].

Some of the studies have reported substitutional doping in III-V semiconductors through ion implantation [11–14], which makes it the topic of interest. An improvement in activation efficiency of p-dopant has also been reported in Be ion-implanted p-GaN [15], which can increase the carrier concentration and reduce contact resistance in GaN LED [16, 17]. The RTA treatment of ion-implanted materials can also result in chemical reactions of the chemically active ions with the lattice elements. However, most of the studies focus on the effect of doping on the optical and electrical properties of material barely giving any attention to the possibility of the formation of new chemical species [18–23]. In this work, the formation of $\beta$-Be$_3$N$_2$ nanocrystallites after RTA at 1100 °C has been confirmed in Be-implanted GaN by careful HRTEM and Raman spectroscopy investigations.

2. Experimental

The substrate used in GaN growth was double face polished $\alpha$-Al$_2$O$_3$ (0001) wafer. The GaN epilayer of 2 $\mu$m thickness was grown by low-pressure metalorganic chemical vapor deposition with trimethylgallium and NH$_3$ as sources; and hydrogen and nitrogen as carrier gases. The electron concentration and Hall mobility values of the as-grown GaN sample were in the range of 1–3 $\times$ 10$^{17}$ cm$^{-3}$ and 150–300 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The
GaN sample was implanted at room temperature by a Be ion dose of \(5 \times 10^{14} \text{ cm}^{-2}\) with an energy of 50 keV. After implantation, face-to-face [24] RTA treatment was performed in nitrogen ambient for 40 s at 1100 °C.

The samples were investigated by a high-resolution transmission electron microscope (FEI Tecnai G2 F20) operated at 200 kV with a point-to-point resolution of 2.4 Å. The Raman spectra were obtained by a 532 nm He-Cd laser of LabRAM HR evolution micro-Raman-PL spectroscope, and recorded in backscattering geometry from the growth surface with the light propagating parallel to the c-axis.

### 3. Results and discussion

The cross-sectional HRTEM image of Be-implanted and RTA treated sample is shown in figure 1. The detailed epitaxial structure is clearly observed in the image.

A distinct damage layer can be observed from the top surface to the depths around 293 nm due to Be dose of \(5 \times 10^{14} \text{ cm}^{-2}\) implanted at an energy value of 50 keV. The 33.6 nm deep layer from the surface of GaN is the more seriously damaged layer that forms due to the ion implantation induced amorphization. The depth of 150.1 nm from the surface has the highest ion concentration. The depth of the damage layer is in accordance with the result simulated by SRIM (shown in figure 2), which represent the Be ion depth in the sample. Under the damage layer, an un-implanted GaN layer extends to 2089.3 nm from the top surface. The parts adjacent to the GaN layer are a 100 nm GaN buffer layer and the underlying sapphire substrate in sequence.

Figure 3 shows an HRTEM image with a magnification of 22.5 k, where two different sets of interplanar distances and crystal orientations can be observed. The FFT image is shown in the inset of figure 3.
The interplanar distances 1.365 Å, 1.592 Å, and 2.618 Å in the lower part of figure 3 are indexed as (1 1 2), (1 1 0), and (0 0 2) crystal planes of hexagonal GaN that have typical values of 1.358, 1.595, and 2.593 Å in the standard PDF database, respectively. The relative percentage difference between the interplanar distances are 0.5%, 0.2%, and 1.0%, respectively, within the error of 1.0%. The FFT was obtained using the Gatan Digital Micrograph software. The lower parallelogram in the inset of the figure 3 confirms that the lower part contains crystallites of hexagonal GaN. A characteristic parallelogram consisting of three reciprocal vectors in FFT has the values of 3.857, 6.276, and 7.315 nm⁻¹, with interplanar distances of 2.593, 1.593, and 1.367 Å, respectively, corresponding to the crystal planes (0 0 2), (1 1 0), and (1 1 2) of hexagonal GaN. The intersection angles are 31.73°, 58.27°, and 90° between the planes (1 1 0) and (1 1 2), (0 0 2) and (1 1 2), and (0 0 2) and (1 1 0), respectively. The intersection angles barely show any difference with standard values that are 31.61°, 58.44°, and 90.05° between (1 1 0) and (1 1 2), (0 0 2) and (1 1 2) and (0 0 2) and (1 1 0), respectively. These interplanar distances can be indexed as hexagonal GaN crystals.

However, interplanar distances measured in the upper part of figure 3 are 1.484, 2.587, and 4.947 Å. None of the GaN crystal phases have ever been reported to have an interplanar distance value beyond 3 Å. Considering Be implantation, the interplanar distances were calculated and compared with possible materials and phases. There are three crystal planes (1 1 0), (1 0 0), and (0 0 2) in hexagonal Be₂N₂ having inter-planar distance values of 1.421, 2.460, and 4.847 Å respectively. The lattice parameters a and c have the values 2.841 and 9.693 Å, respectively. The interplanar distances of these three crystal planes are close to the measured values in the upper part of figure 3. The relative percentage difference between 1.484 and 1.421 Å, 2.587 and 2.460 Å, and 4.947 and 4.847 Å are 4.4%, 5.2%, and 2.1%, respectively, that give errors beyond 5.0%. Considering the concurrence of Be₂N₂ and GaN in the same area, it is reasonable to deduce that the interplanar distance of 2.587 Å belongs to GaN, that is close to the 2.593 Å value of the interplanar distance plane (0 0 2) in hexagonal GaN. The relative percentage difference between 2.587 and 2.593 Å is 0.2%. The errors in the interplanar distance between measured and standard values come from stress induced by GaN.

The existence of Be₂N₂ is also supported by the FFT result. The upper parallelogram is shown in the inset of figure 3 where three reciprocal vectors with values of 2.073, 6.796, and 7.093 nm⁻¹ can be observed. The interplanar distances are 4.824, 1.471, and 1.410 Å, that are very close to the crystal faces (0 0 2), (1 1 0), and (1 1 2) of hexagonal Be₂N₂. The intersection angles obtained from FFT are 16.61°, 73.57°, and 90.18° between (1 1 0) and (1 1 2), (0 0 2) and (1 1 2), and (0 0 2) and (1 1 0), respectively. The measured values of intersection angles show almost no difference with theoretical values, that are 16.34°, 73.66°, and 90.00° between (1 1 0) and (1 1 2), (0 0 2) and (1 1 2), and (0 0 2) and (1 1 0), respectively. The interplanar distances belong to hexagonal Be₂N₂ crystals and support our understanding.

Figure 4 shows the Raman spectra under optical excitation by 532 nm He-Cd laser. The Raman spectra (a), (b), and (c) belong to as-grown, Be-implanted, and RTA treated samples, respectively. The E₂ (low) and E₂ (high) modes of GaN are observed at 142 and 568 cm⁻¹, respectively. The peak at 416 cm⁻¹ comes from the underlying sapphire substrate and 734 cm⁻¹ is the A₁ (LO) mode of GaN. A peak at 362 cm⁻¹ is the vacancy-related local vibrational mode [23, 25], that disappears after RTA treatment. The peak at 533 cm⁻¹ is the A₁ (TO) mode of GaN, that is hardly detectable after ion implantation due to the ion implantation damage. Two Raman peaks at

![Figure 3. The HRTEM image of Be-implanted GaN after RTA treatment at 1100 °C. The inset shows an FFT image where the upper and lower parallelograms are formed by using the diffraction spots for GaN and Be₃N₂, respectively.](image-url)
168 and 199 cm$^{-1}$ appeared in the Be-implanted GaN sample after RTA treatment at 1100 °C. Similar Raman modes were previously observed and were assumed to arise from Be-related local vibrations in GaN for the reason that they were absent in Raman spectra of GaN implanted with ions other than Be [20, 23]. There is little work on the Raman spectra of Be$_3$N$_2$ with only some calculations of phonon dispersion along the high line of symmetry in the first Brillouin zone [26, 27]. We assign the 168 and 199 cm$^{-1}$ peaks to Be$_3$N$_2$ formed in Be-implanted GaN as a result of RTA on the basis of phonon dispersion curves reported for Be$_3$N$_2$. The peak at 168 cm$^{-1}$ is in accordance with the top of point K in the first Brillouin zone of Be$_3$N$_2$. We assign the 199 cm$^{-1}$ peak as a combination mode of two modes at 88 and 111 cm$^{-1}$ on point M [26, 27]. These Raman modes confirm the formation of Be$_3$N$_2$ after RTA treatment. It should be noted that the fundamental modes at 88 and 111 cm$^{-1}$ were not detected that can be explained in terms of their weak individual contribution to the change in polarizability but their combination gave rise to a reasonable amount of change in polarizability that led to a detectable combination mode [28].

The Raman modes at 168 and 199 cm$^{-1}$ were only detected by 514.5 nm laser previously and were undetectable by 325 nm laser [20, 23]. The 514.5 nm laser is in off-resonance with the reported band gap of the Be$_3$N$_2$ [29] while the 325 nm laser is in close resonance. The resonance condition enhances the Raman modes only in resonance with the energy of the Raman laser. Many low intensity Raman modes can be successfully detected in off-resonance condition making it even more sensitive compared to resonance Raman spectroscopy [30].

4. Conclusion

In summary, Raman spectroscopy and HRTEM of Be-implanted GaN were carried out. A clear evidence is found for the formation of $\beta$-Be$_3$N$_2$ nanocrystallites from the interplanar distances and intersection angles. The Raman modes at 168 and 199 cm$^{-1}$ experimentally observed for $\beta$-Be$_3$N$_2$ were carefully assigned to $\beta$-Be$_3$N$_2$ for the first time that is well-supported by HRTEM results.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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