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Formation and dissolution of microcrystalline graphite in carbon-implanted GaN

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Two sharp bands at ~ 1350 and $\sim 1600\text{ cm}^{-1}$ were observed in the Raman spectra of carbon-implanted GaN after postimplantation annealing treatments. The intensities of these two bands increased while their full widths at half maximum decreased with increasing annealing temperature. The observation of these two bands indicates the formation of microcrystalline graphite in C-implanted GaN. Hall measurements demonstrated that some dispersed C in GaN acted as acceptors and played a role in reducing electron concentration and Hall mobility. The facts that in 1100°C furnace annealing the intensities of these two Raman peaks decreased rapidly to zero and the resistivity increased by 3 orders of magnitude indicate the dissolution of microcrystalline graphite at this temperature. © 2000 American Institute of Physics. [S0021-8979(00)01320-7]

INTRODUCTION

Recently, GaN has been established as one of the most promising semiconductor materials for blue/ultraviolet light emitting devices and for high-power microwave devices.¹ Ion implantation is an important and mature technology for producing high-density and high-performance electronic devices. Early studies of ion-implanted GaN have concentrated on the investigation of potential *p*-type dopants.^{2,3} Properties of GaN epilayers implanted with many types of ions were reported recently.^{4–8} In most of these studies, rapid thermal annealing (RTA) has been employed to activate the implanted ions and to remove the implantation induced damage. Raman spectroscopy has been used to study GaN epilayers.^{9–11} Although some research work has been carried out on GaN samples implanted or doped by C ions,^{2,5,9,12} understanding the characters of carbon in GaN is very limited.^{13–15} In this article, we report on a study of C-implanted GaN. Formation of microcrystalline graphite in C-implanted GaN, its dissolution at high temperature, and the effects of C dispersed in GaN on electrical properties are reported.

EXPERIMENTAL METHODS

The GaN epilayers with thicknesses of about $1\ \mu\text{m}$ were grown on (0001) sapphire substrates using low-pressure metalorganic chemical vapor deposition with trimethylgallium

and ammonia as sources. The electron concentrations and Hall mobilities of the as-grown GaN samples were in the ranges of $1\text{--}5 \times 10^{17}\text{ cm}^{-3}$ and $60\text{--}230\text{ cm}^2/\text{Vs}$, respectively. The GaN epilayers were implanted at room temperature by C ions with an energy of 40 keV and a dose of $3 \times 10^{15}/\text{cm}^2$. After implantation, RTA at temperatures between 300 and 1300°C or furnace annealing between 500 and 1100°C was performed under a N_2 environment. The Raman measurements were carried out on a Renishaw II spectrometer at room temperature using the 514.5 nm line of an Ar^+ laser as an excitation source. The laser beam was focused onto a spot with a diameter of about $1\ \mu\text{m}$ at the sample surface by using a microscope system. Raman spectra were collected in the backscattering configuration from the growth surface with light propagating in a direction parallel to the *c* axis of GaN epilayers. Hall measurements were carried out at room temperature by BIORAD HL5500 equipment.

RESULTS AND DISCUSSIONS

Figures 1(a), 1(b), and 1(c) show, respectively, the spectra of an as-grown GaN sample, an as-implanted GaN sample, and an implanted GaN sample annealed at 800°C for 30 min. For the as-grown sample, as shown in Fig. 1(a), four strong peaks appeared at 144 , 417 , 566 , and 734 cm^{-1} , and three weak features appeared at 1285 , 1392 , and 1467 cm^{-1} . This result is consistent with those reported previously.^{10,11} After C implantation, as shown in Fig. 1(b), three new peaks at 293 , 376 , and 669 cm^{-1} and a broader

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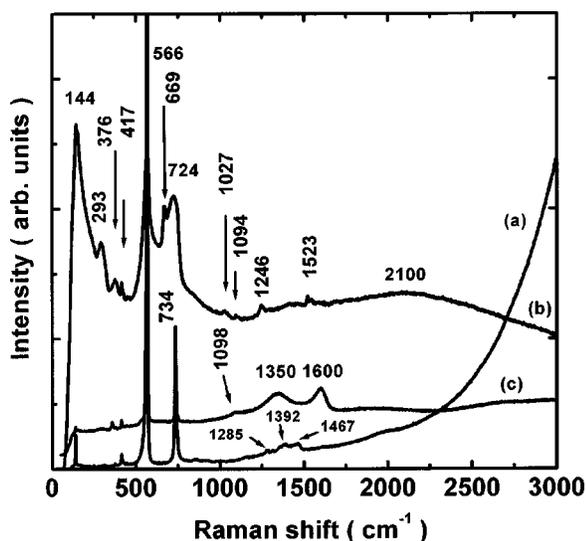


FIG. 1. Raman spectra of: (a) an as-grown GaN sample, (b) a C-implanted GaN sample without annealing, and (c) a C-implanted GaN sample with postimplantation furnace annealing at 800 °C for 30 min.

724 cm^{-1} peak instead of the 734 cm^{-1} peak were observed. The origins of these lines were discussed by Limmer *et al.*⁹ Figure 1(b) shows additional features at 1027, 1094, 1246, and 1523 cm^{-1} , which have not been reported previously. The 1027 and 1094 cm^{-1} peaks may be, respectively, the combination of the 376 and 669 cm^{-1} peaks, and that of the 376 and 724 cm^{-1} peaks. After annealing at 800 °C for 30 min, as shown in Fig. 1(c), most features shown in Fig. 1(b) except for the 376 and 1094 (1098) cm^{-1} bands disappeared, but two new bands around 1350 and 1600 cm^{-1} appeared.

Figures 2(a) and 2(b) show, respectively, Raman spectra of C-implanted and as-grown GaN samples, which were annealed by RTA at different temperatures for 20 s. The ~ 1350 and ~ 1600 cm^{-1} bands increased in intensity and became narrower with an increase of RTA temperature from 400 to 1300 °C. Their peak positions shifted from 1366 and 1588 to 1356 and 1605 cm^{-1} , respectively, as annealing temperature increased from 500 to 900 °C, and remained approximately constant at 1356 and 1605 cm^{-1} , respectively, for annealing temperatures higher than 900 °C. For GaN samples without C ion implantation and annealed at 700 and 1100 °C for 20 s, no peak was observed in the frequency range above 1000 cm^{-1} as shown in Fig. 2(b). This result clearly indicates that these two Raman peaks are related to C implantation.

Figure 3 shows the ratio of the integrated intensity of the ~ 1350 cm^{-1} band to that of the ~ 1600 cm^{-1} band as a function of RTA temperature. This ratio was enhanced rapidly when the RTA temperature increased from 500 to 700 °C. It then decreased as the RTA temperature increased further. Figure 4 shows Raman spectra of C-implanted GaN samples subjected to both RTA and furnace annealing at 800 and 1100 °C for several different annealing times. For the sample annealed at 800 °C, annealing time affected only slightly the intensities and shapes of both bands. However, for the sample annealed at 1100 °C, the intensities of both the bands decreased rapidly with an increase of annealing time. Both

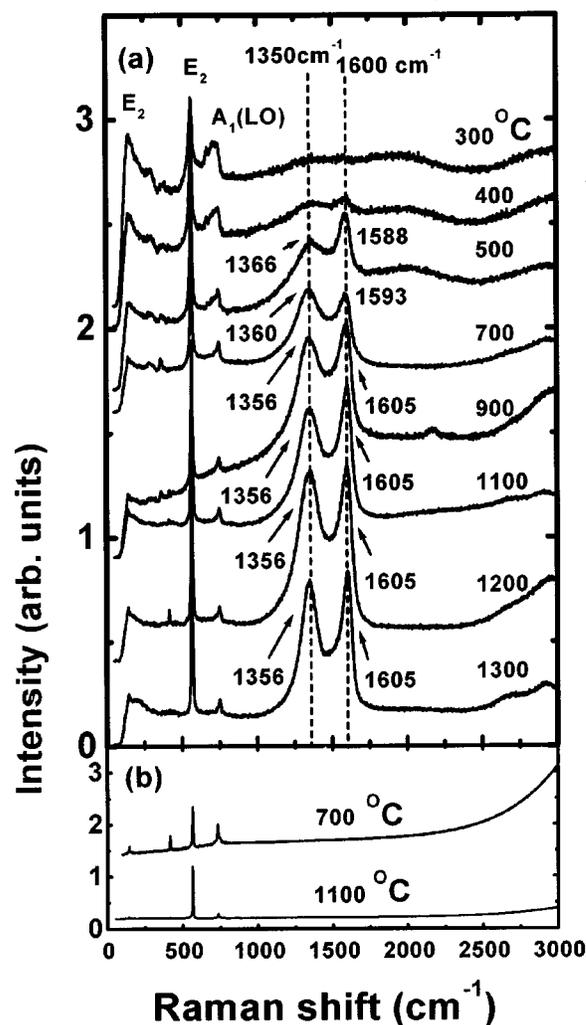


FIG. 2. Raman spectra of: (a) C-implanted GaN samples subjected to RTA with temperatures between 300 and 1300 °C and of (b) two control samples subjected to RTA at 700 and 1100 °C. The RTA time is 20 s for both (a) and (b). The intensities of all spectra are normalized with the E_2 (high) peak intensities taken as a constant.

Raman bands disappeared completely at an annealing time of 20 min.

Figure 5 shows electron concentration and Hall mobility for a C-implanted GaN sample as functions of the furnace annealing temperature and those for the GaN sample before C implantation. The electron concentration and Hall mobility of the GaN sample before C implantation were $1.9 \times 10^{17} \text{cm}^{-3}$ and $105 \text{cm}^2/\text{Vs}$, respectively, while for the sample implanted by C ions they decreased strikingly as the furnace annealing temperature increased from 500 to 1000 °C.

Large single crystal graphite has a single high-frequency band, the *G* band, at about 1580 cm^{-1} .^{16,17} An additional band appears around 1350 cm^{-1} in microcrystalline and disordered graphite known as the *D* band, which is attributed to phonons with wave vectors near the *K* points on the Brillouin zone boundary and is active in small crystallites or on the boundaries of large crystallites. We consider that the features at ~ 1600 and ~ 1350 cm^{-1} observed in the C-implanted GaN correspond, respectively, to the *G* and *D*

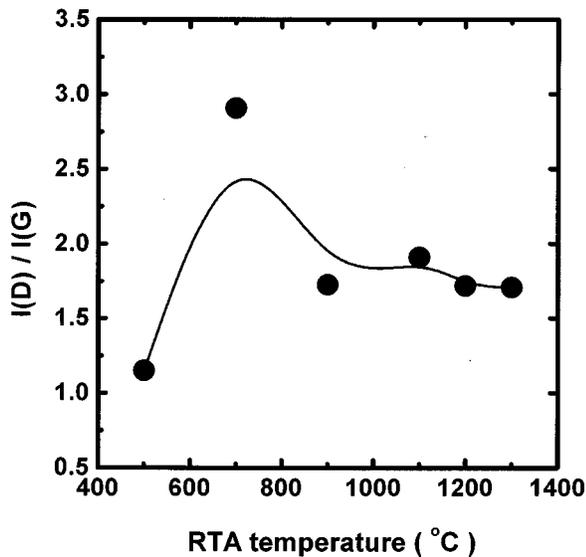


FIG. 3. Ratio of the integrated intensity of the $\sim 1350 \text{ cm}^{-1}$ band to that of the $\sim 1600 \text{ cm}^{-1}$ band as a function of RTA temperature.

bands of microcrystalline graphite arising from C implantation and a postimplantation annealing. One of the possibilities is that the implanted carbon ions diffuse to the regions of dislocations and form microstructures there. We note that Moll *et al.*¹⁸ reported two bands at 1585 and 1355 cm^{-1} in the Raman spectra for C-implanted GaAs and InP with wave numbers close to the values reported here.

Compared to the *D* and *G* bands reported by Moll *et al.*,¹⁸ as shown in Fig. 2(a), the ~ 1350 and $\sim 1600 \text{ cm}^{-1}$ bands, especially those of the samples subjected to RTA with

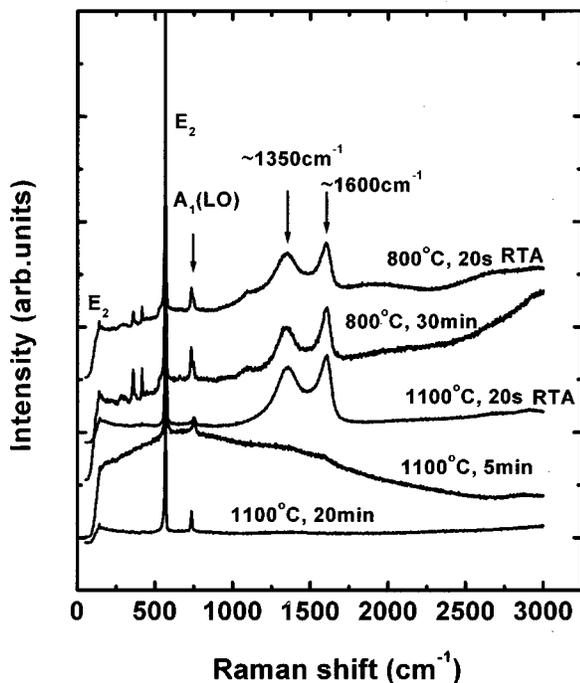


FIG. 4. Raman spectra of C-implanted GaN samples thermally treated at 800 and 1100 °C by a RTA with time of 20 s or a furnace annealing for 5, 20, or 30 min.

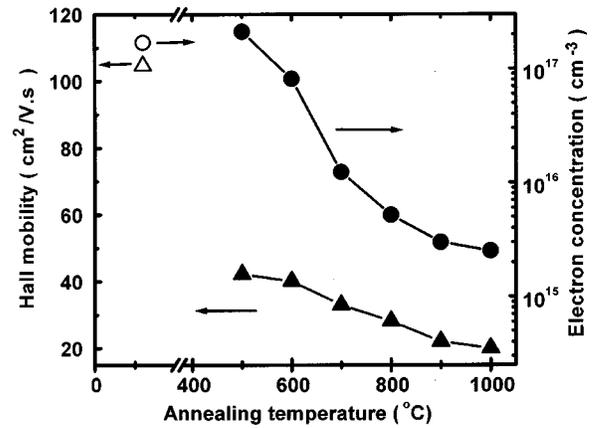


FIG. 5. Electron concentrations and Hall mobilities of a GaN sample before C-implantation (shown by an open circle and an open triangle, respectively), and after postimplantation furnace annealing at temperatures in the range of 500–1000 °C for 20 min (shown by full circles and full triangles, respectively).

temperatures higher than 700 °C, are much narrower. This result indicates that the graphite-like clusters in C-implanted GaN may have much less bond-angle distortion and/or much higher ingredient of single-crystalline graphite in comparison with those in C-implanted GaAs and InP.¹⁸

The integrated intensity ratio of the *D* and *G* bands, $I(D)/I(G)$, is roughly proportional to the ratio of the momentum nonconserving-to-conserving phonon number.¹⁹ As shown in Fig. 3, this ratio reached a maximum at a RTA temperature of 700 °C, and decreased as the RTA temperature increases further. The increase of this ratio indicates the crystallization of amorphous carbon clusters and an increment in number of microcrystalline graphite clusters with increasing RTA temperature. However, further increase of RTA temperature decreased this ratio due to the growth in dimensions of the clusters, which led to an increase in the effect of momentum conservation. The disappearance of the 1350 and 1600 cm^{-1} bands with an increase of furnace annealing time at 1100 °C, as demonstrated in Fig. 4, could be attributed to the dissolution of graphite-like crystallites and pronounced C diffusion at this temperature, which is far lower than the fusion temperature 3500 °C of bulk graphite. Compared with those of the as-grown sample, the electron concentration of the sample implanted by C ions and then annealed at 500 °C by a furnace increased slightly, while its Hall mobility decreased by a factor of 2. The explanation for these two facts is that besides the C-related acceptors, the C-related shallow donors appeared after C-implantation and 500 °C annealing, which is consistent with the conclusion that C in GaN can exist as shallow donors.¹² As furnace annealing temperature increased from 500 to 1000 °C, the electron concentration was decreased by nearly 2 orders of magnitude and the Hall mobility to a half. However, for a control GaN sample without C ion implantation, its Hall mobility and electron concentration were decreased by factors less than 20% after a 1000 °C furnace annealing. Based on these results, we consider that after postimplantation annealing a part of the C implanted in GaN turns into microcrystalline graphite, and the other part of C exists in a dispersive

form, e.g., in a substitutional or an interstitial site. Some C atoms also act as acceptors and compensate for the shallow donors, and this results in pronounced decreases in both electron concentration and Hall mobility. Annealing at 1000 °C for 20 min, the resistivity increased to $1.2 \times 10^2 \Omega \text{ cm}$. By further annealing at 1100 °C, the resistivity increased by more than 3 orders of magnitude to more than $10^5 \Omega \text{ cm}$, which is too high to be measured exactly. This fact can be explained by dissolution of microcrystalline graphite, which greatly enhanced the compensation effect.

CONCLUSIONS

Two bands at ~ 1350 and $\sim 1600 \text{ cm}^{-1}$ were observed in the Raman spectra for C-implanted GaN samples annealed between 400 and 1300 °C by RTA. These two bands are attributed to the existence of microcrystalline graphite in C-implanted GaN. C implantation and a postimplantation annealing at temperatures in a range of 500–1000 °C resulted in acceptors in GaN, which compensated for the shallow donors and strongly decreased electron concentration and Hall mobility. The results of Hall effect measurements are consistent with those of Raman scattering, and both experiments indicate a common conclusion that 1100 °C is the critical temperature for dissolution of microcrystalline graphite in GaN.

ACKNOWLEDGMENT

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