Activation of Beryllium-Implanted GaN by Two-Step Annealing

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ABSTRACT

For the first time, *p*-type doping through beryllium implantation in gallium nitride was achieved by using a new annealing process, in which the sample was first annealed in forming gas (12% H_2 and 88% N_2), followed by annealing in pure nitrogen. Variable temperature Hall measurements showed that sheet hole concentrations of the annealed samples were about 1×10^{13} cm^{-2} with low hole mobilities. An ionization energy of 127 meV was estimated with a corresponding activation efficiency of ~ 100%. SIMS results revealed a relationship between the enhanced diffusion of Be and activation of the acceptors.

INTRODUCTION

A critical issue in the fabrication of gallium nitride (GaN) devices is the achievement of significant and controllable *p*-type doping. It still remains a challenge because of the high *n*-type autodoping background present in as-grown materials and the large ionization energy of acceptors, such as Mg, Zn and Cd.[1] The principal *p*-type dopant used for GaN is Mg with an ionization energy of 150-165meV.[2] Such a large acceptor ionization energy is problematic and two to three orders of magnitude higher atomic doping level of Mg must be incorporated into GaN in order to achieve the desired hole concentration at room temperature.[3] Although Zn and Cd are conventionally used as *p*-type dopants in the growth of other III-V compounds, Strite[4] suggested that the *d*-electron core relaxation in these elements is partially responsible for the enhanced depth, making efficient doping at room temperature impossible.

Beryllium (Be) was thought to be a shallower acceptor in GaN due to its large electronegativity and the absence of *d*-electrons. *Ab initio* calculations[5] predicted that Be behaves as a rather shallow acceptor in GaN, with a thermal ionization energy of 60 meV in wurtzite GaN. More evidence from photoluminescence (PL) spectra revealed that Be acts as an acceptor with an optical ionization energy ranging from 90-100 meV,[6,7] 150 meV,[8] to 250 meV.[9] However, the size of Be atoms is so small that it seems more probable for them to stay at interstitial sites (Be$_{int}$) rather than at substitutional sites (Be$_{Ga}$) in GaN. Theoretical calculations[10] also pointed out that the formation energy of Be$_{int}$ is much less than that of Be$_{Ga}$. Interstitial Be behaves like a double donor so that self-compensation is a significant drawback for the use of Be as an acceptor. That is why there is almost no achievement of electrical activiation of Be-doped GaN, except for Brandt *et al*. who obtained high mobility *p*-type materials from Be-O codoped cubic GaN by molecular beam epitaxy.[11]

In this paper, we introduce a new annealing process in which the Be-implanted GaN wafers were first annealed in forming gas, followed by annealing in a pure N_2 atmosphere.

Electrical activation of Be-implanted GaN was observed for the first time. The results confirmed the low activation energy of Be as an acceptor in GaN and also showed the possibility of p-type doping by Be implantation.

EXPERIMENT

The undoped GaN layers used in the experiments were 2μm thick and grown on c-plane sapphire substrates by MOCVD in a multiwafer rotating disk reactor at 1040 °C, with a ~20 nm GaN buffer layer grown at 530 °C in advance. The background n-type carrier concentrations were around 9×10^{16} cm^{-3}. The as-grown layers had featureless surfaces and were transparent with a strong near band-edge luminescence at 3.44 eV at room temperature. Be was implanted[+] into two pieces of the undoped GaN wafer at 40 keV. The doses were 3×10^{14} cm^{-2} and 1×10^{15} cm^{-2}, respectively. Samples of dimensions 6×6 mm^2 were cut from the wafers. Annealing was performed in a RTP system equipped with halogen-tungsten lamps. One set of the implanted samples was sequentially annealed at 900 -1100 °C for 45 s in flowing N$_2$ according to a face-to-face geometry. The other set of implanted samples was annealed in forming gas (12% H$_2$ and 88% N$_2$) first at temperatures ranging from 500 to 1100 °C and then in flowing N2. Hall effect measurements were conducted at room and variable temperatures with a magnetic field of 0.32 Tesla. Indium dots were alloyed at the corners of each sample according to the Van der Pauw geometry. Secondary ion mass spectrometry (SIMS) analyses were carried out in a CAMECA ims-6f microscope. An O$_2^+$ beam of 200 nA and 8 keV impact energy was used to sputter the samples. The quantification of the H concentration was not available due to the lack of reference. However, the H$^+$ intensities in all the samples have been normalized with respect to N$^+$, and therefore were comparable.

RESULTS AND DISCUSSION

From the variable temperature Hall measurements, a plot of the sheet carrier concentration/ temperature product ($p_s T^{-3/2}$) vs. reciprocal temperature can be constructed. Figure 1 shows such a plot for a Be-implanted GaN sample annealed at 600 °C and 10 s in forming gas first, followed at 1100 °C and 45 s in N$_2$. As shown by Gotz et al.,[12] the normal slope analysis in a linear region of the carrier concentration alone versus reciprocal temperature data could yield around 1/3 more than the real activation energy. We think the Arrhenius plot of the sheet carrier
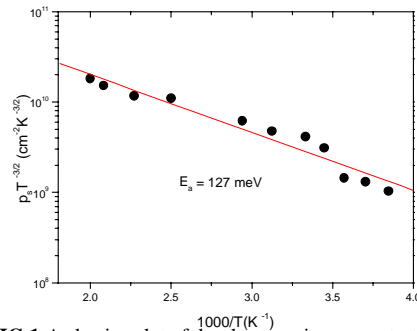
FIG.1 Arrhenius plot of the sheet carrier concentration/ temperature product of Be-implanted GaN annealed in forming gas first, followed in N$_2$, the dose is 3×10^{14} cm^{-2}

[+] The implantation was performed by Implantation Science Corporation, Wakefield, MA, USA

concentration/temperature product vs. the inverse temperature is more appropriate to estimate the ionization level of Be. Under nondegenerate conditions, the hole concentration can be expressed as the following relation: $p \propto p_o T^{3/2} exp(-E_a/kT)$, where p_o is the acceptor concentration and E_a is the activation energy of the acceptors. So, $ln(pT^{3/2})$ should be proportional to the inverse T. Due to non-uniformity of the implanted atoms in the substrate layer, here we use the sheet carrier concentration p_s to plot, instead of p. From Figure 1, the ionization energy of Be in GaN is calculated to be 127 meV, which is lower than that of Mg and Ca reported for implanted GaN.[2,13] Based on the ionization energy estimated above, only 0.73% of Be acceptors would be ionized at room temperature. The activation efficiency can thus be estimated to be around 100% for this sample (considering $p_s = 2.14 \times 10^{13}$ cm^{-2} at room temperature), if the activation efficiency is defined as sheet carrier concentration /(dose×ionization rate). The activation efficiency of Be is similar to that of Ca.[13]

The results of room temperature Hall measurement are summarized in Table I. Several remarkable things should be pointed out. (i) The implanted samples without post-annealing process still showed n-type conductive characteristics with a bit of reduction in electron concentrations, unlike most implanted GaN samples which had high resistivities due to defect states within the band gap that act as traps for the carriers. This may be the results of less damage produced by the smaller mass of Be, low implantation energy (40 KeV) and the resistance of GaN materials to damage by implantation, with considerable dynamic recovery of implantation-induced disorder. High-resolution x-ray diffractometry (HRXRD) was performed to detect the implantation damage. There was no difference in the rocking curves between the as-grown sample and the as-implanted sample. However, it should be noted that HRXRD results could not demonstrate conclusively that the implantation damage was not significant because HRXRD is not very sensitive to implant damage for the lower dose

TABLE I. Room temperature Hall effect data of GaN samples

Sample*	Annealing condition	Type & sheet carrier concentration (cm-2)	Mobility (cm^{2}V^{-1}s^{-1})
416G	as-grown	$n \sim 1.98 \times 10^{13}$	96
416I	as-implanted	$n \sim 8.4 \times 10^{12}$	63
416D5	1100 °C and 45 s in N$_2$	$n \sim 1.12 \times 10^{13}$	98
416D10	700 °C and 10 s in forming gas; then at 1100 °C and 45 s in N$_2$	high resistivity (p-type indicated from the thermal probe measurement)	
417G	as-grown	$n \sim 1.7 \times 10^{13}$	107
417I	as-implanted	$n \sim 8.6 \times 10^{12}$	122
417H5	1100 °C and 45 s in N$_2$	$n \sim 8.6 \times 10^{12}$	122
417H10	700 °C and 10 s in forming gas; then at 1100 °C and 45 s in N$_2$	$p \sim 2.0 \times 10^{13}$	3
417H14	600 °C and 10 s in forming gas; then at 1100 °C and 45 s in N$_2$	$p \sim 2.14 \times 10^{13}$	0.8

*The doses for Sample 416 series and 417 series are 1×10^{15} cm^{-2} and 3×10^{14} cm^{-2}, respectively

sample. (ii) The new annealing process for the high dose (1×10^{15} cm^{-2}) implanted samples produced high-resistivity material. This is probably because, besides the native donors and interstitial Be, more defects were introduced by the higher dose implantation, which compensated the effects of the activated acceptors. This is similar to the case of high Mg doping in GaN.[14] (iii) *p*-type doping was achieved for the lower dose (3×10^{14} cm^{-2}) implanted samples, with a sheet hole concentration around 10^{13} cm^{-2}. To confirm the realization of *p*-type doping, thermal probe measurements were performed. We used Mg-doped *p*-type GaN and undoped *n*-type GaN samples as references. The results were consistent with the Hall measurements, thus confirming that the Be-implanted and annealed samples were indeed *p*-type.

Figure 2 depicts the SIMS profiles of Be and H for different samples. Fig.2(a) shows the depth profiles of Be and H in the as-grown sample. The measured Be concentration was due to a background level noise governed by the intrinsic impurity and the detection limit of our SIMS measurement conditions. The depth profile of Be in the as-implanted sample exhibited a peak at a depth of 120 nm as shown in Fig.2(b). The H profile in this sample was almost the same as that in the as-grown sample. There was no significant channeling tail of Be, unlike that in the Be as-implanted samples (45 keV, 5 × 10^{14} cm^{-2}) in REF 15. We think the differences are from the implantation process, such as beam divergence or other random factors, but probably not from some factors like energy and dose, which are similar to ours. After annealing at 1100 ^{o}C for 45 s, the peak was nearer the surface than that in the as-implanted sample. The projected range was 73 nm (Fig.2(c)). The H profile remained similar. The Be redistribution in this case can be attributed to defect-assisted diffusion.[16] It is noted that some groups[15,17] did not see measurable redistribution of Be in GaN. In Fig. 2(d), the Be and H profiles of the sample annealed with the new process were substantially different from the others. In the top 230 nm layer, the Be profile showed a plateau-like shape, at a concentration of ~1.2×10^{19} cm^{-3}.
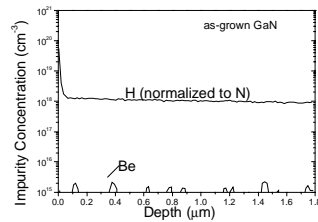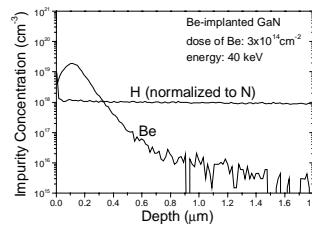

Fig.2 (a)

Fig.2 (b)

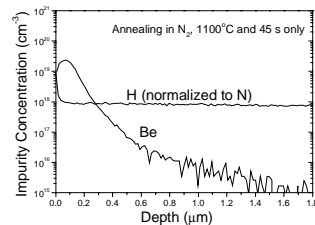Fig. 2 (c)

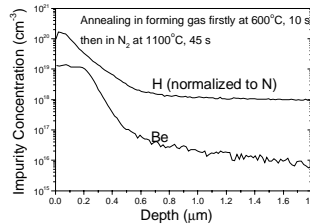

Fig. 2 (d)

At depths beyond 0.5 μm, the Be level was much higher than that in the as-implanted sample and N_2-annealed sample, indicating enhanced in-diffusion of Be. In addition, accumulation of H was observed in the near-surface region, where the H concentration was one to two orders of magnitude higher than the background level. From the study of thermal stability of hydrogen in [2]H-implanted p-type GaN,[18] the diffusion of the deuterium started at a lower temperature of about 500-700 ^{o}C and Mg-H complexes were formed, but these were completely gone by 1000 ^{o}C. However, for our samples, even an 1100 ^{o}C annealing could not entirely break the bonds of potential H complexes and remove the H. From the analysis of Hall and thermal probe measurements, it seems that there exists some relationship between the enhanced diffusion of Be and the activation of the acceptors, similar to the case of Zn diffusion and the optical activation of acceptors in Zn-implanted GaN.[19]

The effect of the new annealing process on Be activation can be tentatively explained as follows. After implantation, there are many Be atoms at interstitial sites, which could easily form a large concentration of substitutional-interstitial (SI) Be-related complexes. Annealing in an atmosphere containing hydrogen might cause the formation of Be_{int}-H complexes first. The Be_{int}-H complexes can move into Ga vacancies (V_{Ga}) more easily and are then converted to Be_{Ga}-H-N complexes. The energy required to break the H-bonds in the Be_{Ga}-H-N complexes might be lower than that needed to move the Be_{int} directly to the substitutional sites during conventional annealing in N_2 only. The subsequent annealing in flowing N_2 will then depassivate the complexes and activate the implanted Be. An independent inference from a first-principles calculation[20] also pointed out that an annealing stage in an ambient including hydrogen before conventional annealing in N_2 would improve activation of p-type dopants in GaN.

CONCLUSION

In conclusion, we present a new annealing process and have observed significant improvement of activation in Be-implanted GaN for the first time, demonstrate the possibility of p-type doping in GaN through Be implantation and confirm that Be has a shallow acceptor level in GaN. Further optimization of annealing conditions will be investigated to improve the properties of Be-implanted GaN.

ACKNOWLEDGEMENTS

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