P- AND N-TYPE IMPLANTATION DOPING OF GaN WITH Ca AND O

J. C. ZOLPER,^a R. G. WILSON,^b S. J. PEARTON,^c and R. A. STALL^d^a Sandia National Laboratories, Albuquerque, NM 87185-0603^b Hughes Research Laboratory, Malibu CA 90265^c University of Florida, Depart. of Materials Science and Engineering, Gainesville, FL 32611^d Emcore Corp., Somerset, NJ 0887

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ABSTRACT

III-N photonic devices have made great advances in recent years following the demonstration of doping of GaN p-type with Mg and n-type with Si. However, the deep ionization energy level of Mg in GaN (~160 meV) limits the ionized of acceptors at room temperature to less than 1.0% of the substitutional Mg. With this in mind, we used ion implantation to characterize the ionization level of Ca in GaN since Ca had been suggested by Strite [1] to be a shallow acceptor in GaN. Ca-implanted GaN converted from n-to-p type after a 1100 °C activation anneal. Variable temperature Hall measurements give an ionization level at 169 meV. Although this level is equivalent to that of Mg, Ca-implantation may have advantages (shallower projected range and less straggle for a given energy) than Mg for electronic devices. In particular, we report the first GaN device using ion implantation doping. This is a GaN junction field effect transistor (JFET) which employed Ca-implantation. A 1.7 μm JFET had a transconductance of 7 mS/mm, a saturation current at 0 V gate bias of 33 mA/mm, a f_t of 2.7 GHz, and a f_{max} of 9.4 GHz. O-implantation was also studied and shown to create a shallow donor level (~25 meV) that is similar to Si. SIMS profiles of as-implanted and annealed samples showed no measurable redistribution of either Ca or O in GaN at 1125 °C.

INTRODUCTION

The III-V nitride-containing semiconductors InN, GaN, and AlN and their ternary alloys are attracting renewed interest for application to visible light emitters [2,3] and as the basis for high-power or high-temperature electronics [4,5]. Their attractive material properties include bandgaps ranging from 1.9 eV (InN) to 6.2 eV (AlN), an energy gap ($E_g(\text{GaN}) = 3.39 \text{ eV}$) close to the short wavelength region of the visible spectrum, high breakdown fields, high saturation drift velocities and relatively high carrier mobilities [6,7].

A primary reason for the recent advances in III-N based photonic devices was the demonstration of p-type doping of GaN during MOCVD growth followed by a dehydrogenation anneal to activate the Mg acceptors [8,9]. Unfortunately, the ionization level of the Mg acceptor in GaN is approximately 150 to 165 meV [9] thus limiting the electrically active acceptors at room temperature to ~ 0.3% of the substitutional Mg. The other common column II acceptors used in III-V semiconductors, namely Be, Zn, and Cd, are reported to have still larger ionization energies than Mg, therefore limiting their effectiveness as p-type dopant species [6]. The demonstration of an acceptor in GaN with a smaller ionization level than Mg would contribute to enhancing the p-type conductivity and reducing resistive losses in p/n junction photonic devices. Along these lines, Strite [1] has presented a theoretical argument for Ca to be a shallower acceptor in GaN than Mg based on d-state electron relaxation effects in GaN and the lack of d-state electrons in Ca. One goal of this paper is to test this theoretical hypothesis experimentally by implanting Ca in GaN and measuring the electrical ionization level. The redistribution of Ca in GaN after high temperature annealing is also studied.

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A second goal of this work is to examine alternative n-type dopants in GaN. N-type doping of GaN during growth [10,11] or by ion implantation [12] has primarily been done using Si which is reported to have a donor ionization level between ~25 and ~60 meV [11,13]. O is of particular interest as a possible alternative n-type dopant due to its position next to N in the periodic table and its suspected role as a background impurity in as-grown GaN [14]. In fact, studies of O introduction in GaN during growth have shown O to act as a donor [14,15]; however, we are not aware of any reports prior to this work on the electrical characterization of O-implanted GaN or on the redistribution properties of O at high temperatures.

We report here on the ion implantation and electrical activation of Ca as an acceptor and O as a donor in GaN. Variable temperature Hall measurements were used to estimate the ionization levels for both dopants. The thermal stability of both species is assessed using secondary ion mass spectrometry (SIMS) profiles of as-implanted and annealed samples. We also reported the first III-N device fabricated with ion implantation doping - a GaN junction field effect transistor.

EXPERIMENTAL

The GaN layers used in the implant doping experiments were 1.5 to 2.0 μm thick grown on c-plane sapphire substrates by metalorganic chemical vapor deposition (MOCVD) in a multiwafer rotating disk reactor at 1040 °C with a ~20 nm GaN buffer layer grown at 530 °C [16]. The GaN layers were unintentionally doped, with background n-type carrier concentrations $\leq 5 \times 10^{16} \text{ cm}^{-3}$. ^{40}Ca or ^{16}O ions were implanted at a dose of $5 \times 10^{14} \text{ cm}^{-2}$ at energies of 180 or 70 keV, respectively, to place the ion peak roughly 100 nm from the surface. One Ca-sample was also implanted with ^{31}P (130 keV, $5 \times 10^{14} \text{ cm}^{-2}$) to study the effect of co-implantation, which has been shown to be required to achieve p-type conduction for Mg-implantation in GaN [12]. SIMS samples were prepared with the same implant conditions except ^{18}O isotopes were used to reduced interference problems with background ^{16}O and improve the sensitivity of the SIMS analysis for O. Samples were annealed for 10 to 15 s in flowing N_2 in a SiC coated graphite susceptor between 900 and 1150 °C to study the electrical activation and redistribution of the dopant species.

RESULTS AND DISCUSSION

Figure 1 is the electrical activation data for Ca-implanted GaN with and without the P co-implantation [17]. An unimplanted and annealed sample is included for comparison. Both the Ca-only and the Ca+P samples convert from n-type to p-type after a 1100 °C anneal. This is slightly higher than the temperature required to achieve p-type conduction in Mg+P implanted GaN [12] and may be the result of more implantation induced damage associated with the heavier Ca-ion. The acceptor activity is seen to continue to increase after annealing at 1150 °C with the P co-implanted sample having a 43% lower sheet resistance and a correspondingly higher sheet hole concentration (1.57 versus $1.14 \times 10^{12} \text{ cm}^{-2}$). Under the same annealing conditions, the unimplanted sample remains n-type with a slight decrease in sheet resistance that may result from the creation of additional N-vacancies or the depassivation of other n-type impurities. The Hall hole mobility of the Ca-only and Ca+P samples was $\sim 7 \text{ cm}^2/\text{Vs}$ after a 1150 °C anneal which is in the range reported for epitaxial Mg-doped GaN [8,9]. Figure 2 is an Arrhenius plot of the sheet hole concentration of the 1150 °C annealed Ca-implanted sample along with similar data for a Mg+P implanted sample with the same dose annealed at 1100 °C [13]. A least squares fit to the data gives an ionization level for Ca of 169 meV and 171 meV for Mg+P in GaN. The higher hole concentration in the Ca-sample may be the result of a more optimum annealing temperature for this sample or a difference in the background, compensating, impurity concentrations.

Fig 1. Sheet resistance versus annealing temperature for Ca-implanted (180 keV, $5 \times 10^{14} \text{ cm}^{-2}$) GaN either with or without a P co-implant. Both samples converted from n-to-p type after a 1100 °C anneal.

FIG 2. Arrhenius plot of the sheet hole concentration for Mg(+P) and Ca implanted GaN. Both samples have an acceptor ionization energy of $\sim 170 \text{ meV}$.

Figure 3 is an Arrhenius plot of the resistance/temperature product of O-implanted GaN annealed at 1050 °C along with data for an unimplanted and annealed (1100 °C) GaN sample. For n-type conduction, an Arrhenius plot of the resistance/temperature product is thought to be more appropriate to account for the potential presence of two band conduction in GaN [18]. O is seen to have an ionization level of 28.7 meV. A similar analysis of Si-implanted GaN yielded an ionization energy of 29 meV [13]. For this ionization energy, 33% of the active donors will be ionized meaning only 3.6% of the implanted O-ions ($n_s = 5.9 \times 10^{12} \text{ cm}^{-2}$) are activated. The low activation of O may be the result of the lighter O-ion not creating sufficient lattice damage, and therefore N-vacancies, for the O to occupy a substitutional N-site. This situation may be improved in the future by using a co-implantation scheme. The low apparent O activation may also be explained by the existence of a second deep level for O in GaN that is associated with an oxygen complex. If this were the case, the electrons in the deep level would remain unionized at room temperature and not contribute to the measured electron density. Note that the unimplanted and annealed material has an activation energy for conduction of 335 eV.

FIG 3. Arrhenius plot of the resistance/temperature product for unimplanted and O-implanted GaN.

FIG 4. SIMS profiles for as-implanted and annealed (1100 °C, 15 s) Ca (180 keV, $4 \times 10^{14} \text{ cm}^{-2}$) in GaN.

FIG 5. SIMS profiles for as-implanted and annealed (1100 °C, 15 s) O (70 keV, $4 \times 10^{14} \text{ cm}^{-2}$) in GaN.

Turning to the thermal stability of Ca and O in GaN, Fig. 4 contains the SIMS profiles for as-implanted and annealed (15 s, 1125 °C) Ca in GaN. Within the resolution of the SIMS measurement ($\sim 20 \text{ nm}$), no measurable redistribution has occurred even for this high temperature anneal. This is similar to the redistribution reported for implanted Mg in GaN [19]. By accounting for the ionization energy level of Ca as described above where only 0.14 % of the Ca-ions are ionized at room temperature, the peak ionized hole concentration is estimated to be $6.2 \times 10^{16} \text{ cm}^{-3}$ based on the peak Ca concentration of $4.44 \times 10^{18} \text{ cm}^{-3}$ in Fig. 4. Although this hole concentration is of the same order as the initial background donor concentration, the actual acceptor concentration is equal to the Ca-concentration in Fig. 4, since, as discussed above, we estimate 100% activation of the implanted Ca ions as acceptors based on a 169 meV ionization energy. Therefore, the unionized Ca-acceptors will compensate the initial background donors and thus allow p-type conduction to be achieved. Figure 5 shows the SIMS profiles for implanted ^{18}O in GaN either as-implanted or annealed at 1125 °C. Here again no measurable redistribution is observed near the peak of the distribution. This is in contrast to dramatic redistribution reported for S, another column VI species, that displayed significant redistribution even after a 600 °C anneal [20]. Based on a conservative estimate of the resolution of the SIMS measurement of 20 nm, an upper limit of $2.7 \times 10^{-13} \text{ cm}^2/\text{s}$ is estimated for the diffusivity of Ca and O in GaN at 1125 °C.

With the demonstration of n- and p-type implantation doping, we have now applied this technology to the fabrication of the first GaN junction field effect transistor (JFET) [21]. Figure 6 shows $I_{\text{DS}}/V_{\text{DS}}$ data for a $\sim 1.7 \times 50 \mu\text{m}^2$ GaN JFET made with a Ca p-type implant and Si n-type implants as represented in the schematic in Fig 7. This device had a maximum transconductance of 7.5 mS/mm at $V_{\text{gs}} = -2 \text{ V}$ and a I_{DS} of 33 mA/mm at 0 V gate bias. The frequency performance of this device was very respectable with a $f_t = 2.7 \text{ GHz}$ and $f_{\text{max}} = 9.4 \text{ GHz}$. These metrics are comparable to reported values for epitaxial GaN MESFETs [22].

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FIG 6: I_{DS} vs V_{DS} for the first GaN JFET. The gate length is $\sim 1.7 \mu\text{m}$.

FIG 7. Schematic of all ion implanted GaN JFET using Ca (p-type) and Si (N-type) ion implantation.

CONCLUSION

Ion implantation can be expected to play an enabling role in advanced devices based on III-Nitride materials. In this paper, we have reported results for implantation doping of GaN with Ca for p-type and O for n-type conduction. Ca is seen to have an estimated ionization energy of 170 meV which is similar to that of Mg, the only other acceptor with $E_a < 200$ meV. Both Ca and O were shown to display no measurable redistribute for an RTA at 1125 °C. The first GaN JFET was also reported which also represents the first III-Nitride based device fabricated with ion implantation doping.

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