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Annealing of ion implanted gallium nitride

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In this paper, we examine Si and Te ion implant damage removal in GaN as a function of implantation dose, and implantation and annealing temperature. Transmission electron microscopy shows that amorphous layers, which can result from high-dose implantation, recrystallize between 800 and 1100 °C to very defective polycrystalline material. Lower-dose implants (down to 5×10^{13} cm^{-2}), which are not amorphous but defective after implantation, also anneal poorly up to 1100 °C, leaving a coarse network of extended defects. Despite such disorder, a high fraction of Te is found to be substitutional in GaN both following implantation and after annealing. Furthermore, although elevated-temperature implants result in less disorder after implantation, this damage is also impossible to anneal out completely by 1100 °C. The implications of this study are that considerably higher annealing temperatures will be needed to remove damage for optimum electrical properties. © *1998 American Institute of Physics.* [S0003-6951(98)00710-4]

GaN and other group III-nitrides are currently the subject of intense interest as a result of their attractive properties for the fabrication of a range of optoelectronic devices such as blue–green LEDs, lasers and detectors,[1–4] as well as electronic devices for high power and high temperature operation.[5,6] For integration of such devices into circuits, a selective-area doping technology is required and ion implantation is attractive because of its wide acceptance in the semiconductor industry. However, ion implantation creates lattice damage which must be removed by an annealing step before the implanted dopants are rendered electrically active.[7] In other compound semiconductors such as GaAs and InP, implantation results in extensive crystalline damage and even amorphous layers which recrystallise epitaxially during annealing up to 400 °C.[8] However, in both preamorphous and amorphous cases, low temperature annealing leaves a highly defective crystal which must be annealed at considerably higher temperatures (up to 900 °C) to fully remove all defects and activate dopants.[8–10]

In GaN, recent studies[11–14] have indicated that activation of both n- and p-type dopants can be achieved by annealing up to 1100 °C but results are variable and the electrical properties are far from optimum. Consequently, there is an urgent need to carry out detailed studies on the structural nature of implantation damage in GaN and its removal during annealing. There have been a few recent studies in this regard,[14–17] but no systematic examinations of the structure of implant damage and its annealing behavior. For example, we have previously shown that GaN is quite resistent to damaging by implantation, with considerable dynamic recovery of implantation-induced disorder even during liquid nitrogen temperature implantation.[15] Despite such dynamic annealing, the residual disorder following implantation is significant and amorphous layers can be generated at very high doses ($eg>10^{16}$ cm^{-2} doses of Si at 90 keV).[15] It is also clear that high dose, preamorphous damage cannot be significantly reduced by annealing at 1100 °C.[14] Furthermore, attempts to utilize elevated temperature implants to reduce implant damage and improve activation during subsequent annealing were not substantially successful.[17] In the present study, we have examined the ability to remove implantation damage at temperatures up to 1100 °C, concentrating on the degree and nature of disorder rather than electrical activity. Unfortunately, despite some encouraging results from previous activation studies, 1100 °C is not a sufficiently high annealing temperature to adequately remove implantation damage.

The epitaxial GaN layers used in these experiments were 1–2 μm thick, grown on c-axis sapphire substrates by metalorganic chemical vapor deposition in a rotating disk reactor at 1040 °C with a 20 nm GaN buffer layer grown at 530 °C.[18] These samples provided excellent quality epitaxial GaN layers, as indicated by a 2 MeV He ion channeling minimum yield of better than 3%, but contained a typical

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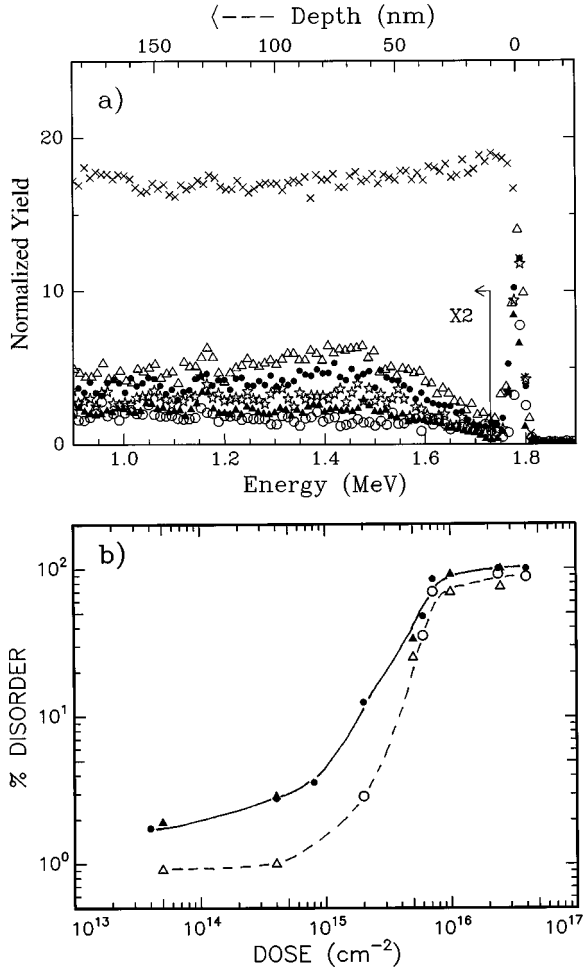

FIG. 1. (a) 2 MeV He^+ RBS-C spectra illustrating the annealing of 90 keV Si ion damage (2×10^{15} cm^{-2}) in GaN at temperatures of 400 °C, 10 min (filled circles), 800 °C, 10 min (stars) and 1100 °C, 30 s (filled triangles). The unimplanted (open circles), as-implanted (open triangles) and random (crosses) spectra are also shown. (b) Peak disorder from RBS-C spectra plotted as a function of dose for 90–100 keV Si ions: as-implanted, liquid nitrogen temperature (filled circles) and room temperature (filled triangles) implants; annealed 1100 °C, (30 s) for liquid nitrogen (open circles) and room temperature (open triangles) implants.

misfit dislocation density of 10^8-10^9 cm^{-2}. Samples were implanted with 90–100 keV Si ions or 350 keV Te ions using the ANU 1.7 MeV tandem ion implanter. The dose range for the Si implantations was from 5×10^{13} to 5×10^{16} cm^{-2}, at liquid nitrogen and room temperatures, and the Te implants were undertaken at a dose of 10^{15} cm^{-2} at 3 temperatures, liquid nitrogen, room temperature and 200 °C. Samples were annealed at temperatures up to 1100 °C under flowing N_2 gas in either a conventional tube furnace (up to 800 °C) or a rapid thermal annealer (RTA) for the higher temperatures. All samples were analyzed by Rutherford backscattering and channeling (RBS-C) using 2 MeV He^+ ions and selected samples were also analyzed by cross-sectional transmission electron microscopy (XTEM).

For samples implanted with Si at liquid nitrogen temperature to doses below about 3×10^{15} cm^{-2}, the GaN was not amorphous after implantation and exhibited a small decrease in damage with increasing annealing temperature. This behavior is illustrated in Fig. 1(a), where RBS-C spectra are shown for 2×10^{15} cm^{-2} Si-implanted GaN at liquid nitrogen temperature and annealed at 400, 800, and 1100 °C.

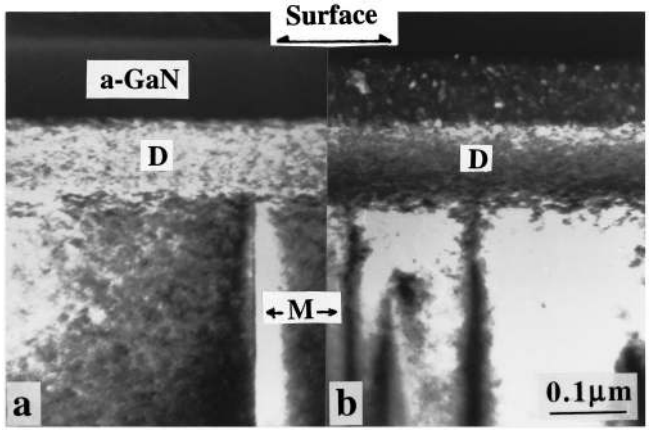

FIG. 2. XTEM micrographs showing the structure for a dose of 4×10^{16} cm^{-2}, 90 keV Si ions at liquid nitrogen temperature: (a) as-implanted and (b) annealed 1100 °C for 30 s. Note the amorphous (a-GaN) layer in (a) and the deep defects (D) below both the a-GaN layer in (a) and the polycrystalline layer in (b). Note also the as-grown misfit dislocations (M).

In this case, even at 1100 °C, RBS-C shows that the damage is not completely removed. For lower Si doses down to 5×10^{13} cm^{-2}, damage removal is more extensive during annealing, but the damage is still not completely removed even at 1100 °C. On the other hand, for Si doses greater than about 5×10^{15} cm^{-2}, annealing up to 1100 °C does not result in any appreciable reduction in damage as observed in RBS-C spectra. Figure 1(b), which shows the peak damage from such RBS-C spectra as a function of Si dose for as-implanted and 1100 °C annealing, illustrates this behavior. Most of the data in Fig. 1(b) refer to liquid nitrogen implants, but the limited data at room temperature, where the initial damage is usually lower, show similar trends.

For doses greater than 10^{16} cm^{-2} shown in Fig. 1(b), the RBS-C spectra show that the disorder reaches the 100% level, which indicates the formation of an amorphous layer after implantation.[18] It is interesting to examine the annealing behavior of such layers and this is revealed in the XTEM micrographs in Fig. 2. Figure 2(a) shows the as-implanted disorder for a Si dose of 4×10^{16} cm^{-2} (liquid nitrogen implant) and reveals a thick amorphous layer with a dense, deeper band of extended defects (D) in crystalline GaN. Note the misfit dislocations (M) which thread towards the surface from the underlying GaN. When this high dose sample is annealed at 1100 °C, Fig. 2(b) shows that the amorphous layer recrystallizes as polycrystalline GaN, with no detectable epitaxial growth. The underlying disorder is observed to coarsen but is otherwise unchanged. Thus the XTEM observations are consistent with the RBS-C data in Fig. 1(b), where the disorder is only marginally reduced at 1100 °C. Further comparison of RBS-C data and XTEM (not shown) indicates that crystallization occurs between 800 and 1100 °C.

The effect of implantation temperature on implantation-induced disorder and its removal is illustrated in Fig. 3(a) for 350 keV Te implantation to a dose of 10^{15} cm^{-2}. Although there is a significant reduction in disorder as the implant temperature increases, in no case is the damage completely removed by annealing at 1100 °C. RBS-C can also determine the lattice location of the heavier Te atoms in GaN and, in

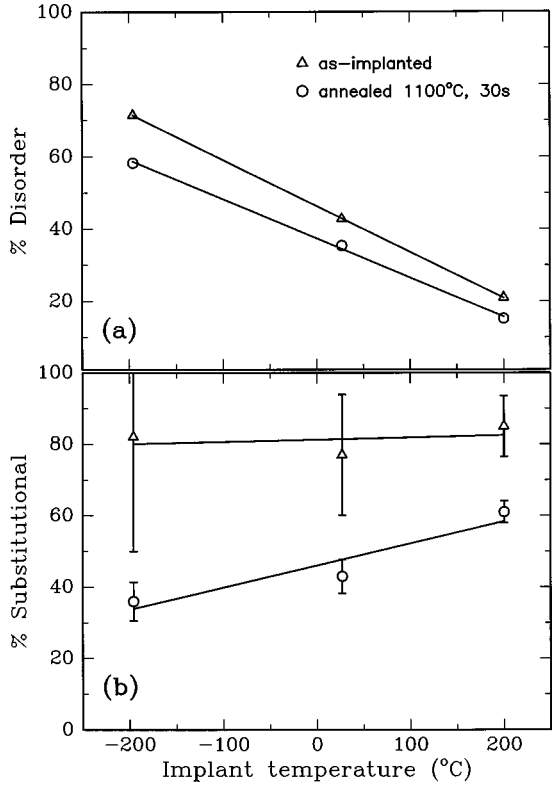

FIG. 3. RBS-C data for 350 keV Te implants into GaN (10^{15} cm^{-2}) as a function of implantation temperature: (a) peak disorder as-implanted (triangles) and after annealing at 1100 °C for 30 s (circles); and (b) Te substitutional fraction for as-implanted (triangles) and 1100 °C (circles).

Fig. 3(b), we show the fraction of implanted Te which occupies lattice sites, as a function of implant temperature. After implantation, a very high fraction (around 80%) of the Te is substitutional at all three temperatures. The large error bars result from the substantial disorder in GaN. The present RBS-C measurements are not able to determine whether this substitutional Te is sitting preferentially on Ga or on N sites, but it is interesting to note that a fraction of Te moves off lattice sites during annealing, although the solubility is still substantial when the very high peak concentration of Te (around 1 at.%) is taken into account. More extensive data on atom location, including the possible movement of the implant species during annealing, will be reported subsequently.

The results presented above have several implications for damage removal and activation of dopants in GaN. First, although recrystallization of amorphous GaN can occur at <1100 °C, the resultant layer is polycrystalline, indicating that amorphization should be avoided during implantation. However, for implant conditions which do not result in amorphization, including elevated temperature implantation, crystalline defects always accompany implantation, and such defects clearly need temperatures >1100 °C to remove them. This is not surprising since the melting point of GaN is very high (2518 °C) and the removal of crystalline defects from other compound semiconductors normally requires temperatures in excess of two thirds of the melting point (in K).[8] What is surprising is that reasonable electrical activity can be obtained in GaN with so much residual damage. In this regard, the atom location measurements are illuminating since they suggest that Te is substitutional despite the disorder. This may indicate that dopants occupy lattice sites during implantation in GaN and basically retain such sites (or preferentially move on to active sites) on annealing, without appreciable interaction with the surrounding defects. Indeed, in contrast to this behavior, dopant–defect interactions are the major cause for deactivation of dopants in GaAs.[9] Thus, in GaN, dopants can be activated at low annealing temperatures but carrier mobilities are very low as a result of residual damage.[14] In this regard, we have recently shown that improved electrical activity and mobility can be obtained by annealing Si-implanted GaN at 1300 °C.[19] However, the AlN cap used to protect the GaN from dissociation begins to decompose at 1300 °C and an improved encapsulation method will be needed for annealing at higher temperatures

In conclusion, we have shown that, for implant temperatures up to 200 °C, annealing temperatures up to 1100 °C are insufficient to completely remove implant damage. Even Si implant doses below 10^{14} cm^{-2} leave residual damage and this probably accounts for low carrier mobilities obtained in previous studies. Heavily disordered but preamorphous GaN is not removed on annealing to 1100 °C, whereas amorphous GaN layers recrystallize to a polycrystalline structure by 1100 °C. Te atoms are highly substitutional and, although they appear to move off lattice sites somewhat on annealing, the solubility remains very high (of the order of 1 at.%).

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