Enhanced dynamic annealing in Ga\(^+\) ion-implanted GaN nanowires

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Ga\(^+\) ion implantation of chemical-vapor-deposited GaN nanowires (NWs) is studied using a 50-keV Ga\(^+\) focused ion beam. The role of dynamic annealing (defect-annihilation) is discussed with an emphasis on the fluence-dependent defect structure. Unlike heavy-ion-irradiated epitaxial GaN film, large-scale amorphization is suppressed until a very high fluence of \(2 \times 10^{16}\) ions cm\(^{-2}\). In contrast to extended-defects as reported for heavy-ion-irradiated epitaxial GaN film, point-defect clusters are identified as major component in irradiated NWs. Enhanced dynamic annealing induced by high diffusivity of mobile point-defects in the confined geometry of NWs is identified as the probable reason for observed differences. © 2003 American Institute of Physics.

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III–V nitrides in general, and specifically GaN, have been subjects of extensive research due to their very important optoelectronic applications.\(^1\) Catalytic growth of hexagonal GaN \((h\text{-GaN})\) nanowires (NWs) has opened up avenues for their application as one-dimensional (1-D) nanodevices.\(^2\) The device application of these materials demands a complete understanding of the defects generated during the growth in thermal equilibrium conditions, as well as in nonequilibrium conditions with ion bombardment as indispensable processing steps. A detailed, systematic study of ion-irradiation damage has been carried out in epitaxially grown GaN \((\text{e.pi-GaN})\) with various ions except the Ga\(^+\) ions.\(^3\) Irradiation damage created by heavy ions with high nuclear energy loss revealed the formation of mostly extended (planar) defects originating from the large cascade (multiple displacement sequence of collision events). A sigmoidal distribution of defect-clustering is reported, with amorphization nucleating on the surface in the initial fluences. Large-scale amorphization is reported at high fluxes. However, the chemical effects of implanted ions are doubted by the authors, suggesting further investigation.\(^4\) This issue can best be resolved by a chemically clean Ga\(^+\) (self) ion-irradiation process in GaN. Self-ion-implantation is studied extensively both in elemental \((\text{Si})^5\) and compound \((\text{GaAs})^5\) semiconductors for systematic defect generation and amorphization. In this report, we address the effect of Ga\(^+\) ion-implantation on GaN NWs by focused ion beam (FIB) at room temperature.

GaN NWs (diameter 25–100 nm) were grown in the presence of catalyst by a chemical-vapor deposition technique following vapor–liquid–solid process.\(^5\) The samples were grown at 900 °C on c-Si substrates pre-coated with Au catalyst, using molten gallium as source material and NH\(_3\) (10 sccm) as a reactant gas in a tubular furnace. Ga\(^+\) ion-implantation on these GaN NWs was achieved using a FIB at 50 keV in the fluence range of \(1 \times 10^{14}–2 \times 10^{16}\) ions cm\(^{-2}\). As calculated from the SRIM code,\(^6\) the range of 50-keV Ga\(^+\) in GaN film is 24 nm, with energy dissipation mainly through nuclear energy loss \((dE/dx)_n \sim 2\) keV/nm. In order to keep the damage-area within the volume of even the smallest-sized NW, stable FIB at low energy was preferred over high-energy broad ion beam. Moreover, compared to broad ion beam, FIB is more monoe-nergetic (energy spread <0.2%),\(^7\) leading to a better-defined longitudinal straggling of the collision cascades created by the ions in the 1-D NW. FIB was raster-scanned 400 \(\times\) 400 \(\mu\)m with an ion flux of \(\sim 5 \times 10^{12}\) ions cm\(^{-2}\) sec\(^{-1}\), which is comparable to the reported\(^3,8\) values for irradiated GaN film.

High-resolution scanning electron microscopic (HRSEM) image [Fig. 1(a)] of the pristine NWs shows random growth with no preferential orientation, as reported earlier.\(^2\) The inset of Fig. 1(a) shows one of the smaller NWs with a diameter of 25 nm. Structural study in the pristine NW with high-resolution transmission electron microscopy (HR-TEM) [Fig. 1(b)] confirmed the growth of highly crystalline \(h\)-GaN, with the zone axis lying along [001] direction as calculated from the corresponding diffraction pattern [inset Fig. 1(b)]. The growth of the typical NW was observed to be along [110] direction from the HRTEM image.

A schematic of the irradiation process and TEM observation direction for a single NW is depicted in Fig. 2(a). The surface layer in the irradiated NW is along either one of the sides with similar type of defect accumulation at both sides, shown in the full image of NWs in the inset. Figure 2(b) shows that the amorphous layer is mostly confined to the
surface layer of samples irradiated at a fluence of $1 \times 10^{14}$ ions cm$^{-2}$ lying adjacent to the bulk crystalline zone. The total thickness of the disordered region is 1.5 nm, increasing to 2.5 nm with increasing fluence up to $1 \times 10^{15}$ ions cm$^{-2}$ (not shown in picture). It is worth mentioning that the total range of 50-keV Ga$^+$ in GaN is 24 nm, as discussed earlier. Instead of maximum defect accumulation around 20 nm as indicated in the Monte-Carlo-based SRIM code calculation, a layered accumulation of defects is observed, which starts appearing close to the surface. This discrepancy occurs as the SRIM code does not account for the defect diffusion and annihilation process taking place during the irradiation process in some of the materials for example GaN.

The similar nature of defect-distribution with prominent layer-by-layer features is observed at higher fluences. Figure 3(a) shows the sample irradiated at a fluence of $3.16 \times 10^{15}$ ions cm$^{-2}$, where a short-range order starts appearing on the surface layer. The total thickness of the disordered region increases to $4 \text{ nm}$. Irradiation at a fluence of $5 \times 10^{15}$ ions cm$^{-2}$ shows a great deal of crystalline order in the surface layer [Fig. 3(b)], followed by a wide amorphous region lying adjacent to the bulk crystalline phase. The total thickness of the disordered region increases to $6 \text{ nm}$. The appearance of pronounced crystallinity on the surface layer suggests a strong dynamic annealing as also reported in ion-irradiated epi-GaN.

It has been shown that dynamic annealing (defect-annihilation) processes in $h$-GaN become relatively efficient during heavy-ion bombardment at an optimum fluence. Ion-beam-generated Frenkel pairs, which survive the ultrashort duration quenching ($\sim 10^{-10}$ s) of collision cascades, are mobile in $h$-GaN even at liquid-nitrogen temperature. A vacancy (or interstitial) cluster is likely to experience annihilation by trapping of mobile interstitials leading to an efficient dynamic annealing. Presumably, high diffusivity of mobile point-defects (interstitials) in the high-curvature geometry of NWs makes this effect even more pronounced than that reported for the ion-irradiated epi-GaN.
The dynamic annealing process is a nonequilibrium process, so that the evolving structure never leads to perfect ordering. In fact, other competitive processes can force the structure to be less ordered at a slightly higher fluence, as observed [Fig. 4(a)] for the sample irradiated with a fluence of $1 \times 10^{16}$ ions cm$^{-2}$. The crystallinity of the ordered region adjacent to the amorphous layer reduces, and total thickness of the disordered region increases to 15 nm. The annihilation of defects by this process at low fluences is less efficient [Fig. 2(b)], and the efficiency increases with increasing fluence [Figs. 3(a) and 3(b)]. However, a competitive process of point-defect cluster formation (mostly complexes of vacancies and/or interstitials) with further increase of ion fluence leads to the total process of dynamic annealing to be inefficient again. Further increase in the fluence amorphizes the surface layer completely, as observed [Fig. 4(b)] for the sample irradiated at a fluence of $2 \times 10^{16}$ ions cm$^{-2}$. Accumulation of defect-clusters at high fluences leads to a large-scale amorphization as observed. The electron diffraction pattern corresponding to the large-scale amorphization of the NW is shown in the inset of Fig. 4(b) (top right corner). Total thickness of the disordered region increases to 15 nm, which is close to the range of the energetic ion. It may also be noted that the nature of defect accumulation leading to amorphization does not depend on crystalline orientation of the target material, and hence, will not matter for NWs with different growth directions. Typical results are shown for each fluence in the present study.

To our surprise, for the entire fluence range, we did not observe the presence of extended-defects in the nuclear-energy-loss-dominated Ga$^+$ ion-implantation of GaN NWs at low energy. Close observation of the defect structures in the irradiated samples suggests agglomeration of point-defect clusters as the major component of disorder at high fluences. On the other hand, planar-defects have been reported for the heavy-ion irradiation in epi-GaN, where the nuclear energy loss is predominant. Enhanced dynamic annealing with high diffusivity of mobile point-defects in the NWs might have prohibited the growth of extended-defects in the irradiated samples. Another interesting observation is that the fluence of $2 \times 10^{16}$ ions cm$^{-2}$ for observing a large-scale amorphization in Ga$^+$ ion-irradiated GaN NWs is much higher than that reported ($4 \times 10^{15}$ ions cm$^{-2}$) for heavy ion, for example, 450-keV Au$^+$ irradiation on epi-GaN, which is also a nuclear-energy-loss-dominated phenomenon, and hence comparable with the low-energy Ga$^+$-irradiation process. This may be also be correlated to the absence of extended-defects in the irradiated NWs.

In conclusion, fluence-dependent defect accumulation is studied in the chemically clean Ga$^+$ ion-irradiation on NWs of GaN. Dynamic annealing is observed to play an important role in emphasizing the layer-by-layer structure of defect accumulation in the intermediate fluence range. Larger accumulation of defects with increasing ion fluence and imperfection of the dynamic annealing process lead to disordering in the higher fluence range, and finally induce amorphization in $n$-GaN NWs at a fluence of $2 \times 10^{16}$ ions cm$^{-2}$ owing to agglomeration of point-defect clusters. The growth of extended-defects, reported for heavy-ion-irradiated epi-GaN, is likely to be prohibited in the presence of enhanced dynamic annealing with high diffusivity of mobile point-defects in the NWs, while making them more sustainable under energetic irradiation conditions than that for the films.

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