Hexagonal-to-cubic phase transformation in GaN nanowires by Ga^{+} implantation

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Hexagonal to cubic phase transformation is studied in focused ion beam assisted Ga^{+}-implanted GaN nanowires. Optical photoluminescence and cathodoluminescence studies along with high-resolution transmission electron microscopic structural studies are performed to confirm the phase transformation. In one possibility, sufficient accumulation of Ga from the implanted source might have reduced the surface energy and simultaneously stabilized the cubic phase. Another potential reason may be that the fluctuations in the short-range order induced by enhanced dynamic annealing (defect annihilation) with the irradiation process stabilize the cubic phase and cause the phase transformation. [DOI: 10.1063/1.1760593]

High ionicity in III–V compounds makes GaN thermally stable only in the hexagonal wurtzite (*h*-GaN) structure. Metastable cubic zinc-blend (*c*-GaN) modification of this material is extremely difficult in equilibrium condition. However, growth of epitaxial (epi-) *c*-GaN layer is achieved on different substrates mostly using the nonequilibrium growth conditions.[1] Cubic phase has potential superiority over hexagonal phase for certain device applications and integrity of GaN devices. For example, *c*-GaN shows a higher mobility, resulting from its lower phonon scattering in the higher crystallographic symmetry,[2] and a high *p*-type conductivity.[3] It is also predicted theoretically that the optical gain in *c*-GaN quantum wells might be higher than that in hexagonal GaN wells.[4] The successful production of high quality *h*-GaN nanowires (NWs)[5] using vapor–liquid–solid (VLS) technique opened up the possibility of device application[6] in these one-dimensional systems. However, formation of pure *c*-GaN NW has not so far been demonstrated to utilize the various advantages over the hexagonal phase.

In case of epi-film, the metastable *c*-GaN is formed by providing lattice matching substrates for epitaxial growth and by kinetic (nonequilibrium processing) or thermodynamic stabilization (''shift of equilibrium'' adopting either Ga-rich[1–3] conditions or adding surfactant like As to lower the surface energy)[7] of the metastable phase. For the growth of nanostructures in the VLS process,[8] however, none of these techniques can be effectively adopted to stabilize the metastable cubic phase in a controlled fashion. Instead, one can think of nonequilibrium modification of the nanostructured materials to transform the stable phase to a metastable one using energetic irradiation process.[9]

We report here a phase transformation of GaN NWs from stable wurtzite to metastable zinc-blend structure induced by focused ion-beam (FIB) assisted Ga^{+}-ion implantation. Optical photoluminescence (PL) and cathodoluminescence (CL) studies along with high-resolution transmission electron microscopic (HRTEM) structural studies are performed to confirm the phase transformation.

Randomly oriented GaN NWs were grown by chemical-vapor deposition technique following VLS process. The samples were grown at 900 °C on *c*-Si substrates precoated with Au catalyst, using molten gallium as source material and NH_3 (10 sccm) as reactant gas in a horizontal tubular furnace. Ga^{+} implantation on these GaN NWs was achieved using a FIB at 50 keV in the fluence range of 1×10^{14}–2×10^{16} cm^{-2} with an ion flux of $\sim5\times10^{12}$ $cm^{-2}\,s^{-1}$. Details of ion irradiation process is reported elsewhere.[10] PL measurements were performed using He–Cd laser tuned to 325 nm with an output power of ~10 mW at room temperature. The emission signal was collected by a SPEX 0.85 m double spectrometer and detected by a lock-in-amplifier. Temperature-dependent CL study was performed using a Gatan MonoCL3 system attached to a JEOL JSM-6700F field emission scanning electron microscope (FESEM). HRTEM studies were performed using JEOL JEM-4000EX.

FESEM image [Fig. 1(a)] showed randomly oriented pristine NWs. HRTEM image [Fig. 1(b)] showed formation of wurtzite GaN phase with zone axis lying along the [001] direction as calculated from the corresponding diffraction pattern [inset to Fig. 1(b)]. The growth of the typical NW was observed to be along [100] direction.

Room temperature (RT) PL study of the pristine NWs is shown in Fig. 2(a). A small peak around 3.1 eV might correspond to longitudinal optical (LO) phonon replica mode of the donor–acceptor pair for cubic phase.[5,11] The minor cubic phase could be stable as stacking faults embedded in the *h*-GaN NW.[5] Intense peak at 3.42 eV closely corresponded

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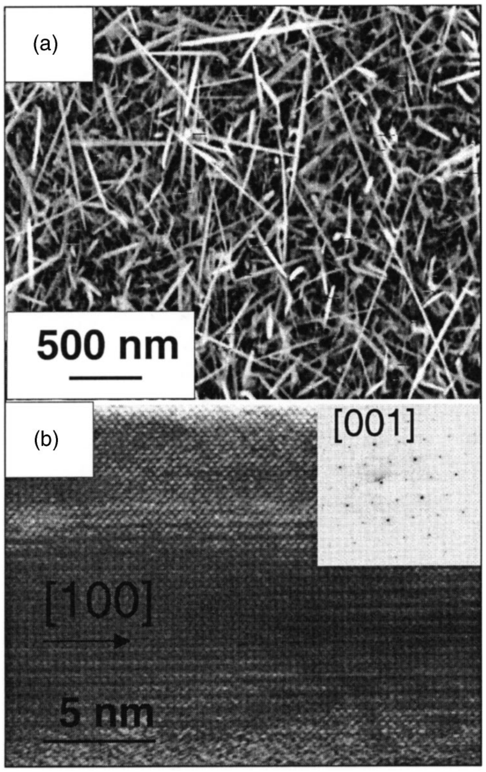

FIG. 1. (a) FESEM image showing randomly oriented pristine NWs. (b) HRTEM lattice image of the pristine GaN NW and corresponding SAED in the inset, showing formation of wurtzite GaN phase with zone axis lying along [001] direction. The growth direction is along [100] direction.

to direct band-to-band transition (E_g) energy of h-GaN confirming presence of predominant wurtzite phase in the pristine NWs. After FIB irradiation with 50 keV Ga^+ we observed continuous deterioration of intensities for both peaks [Fig. 2(a)] with increasing fluence. Most interestingly, intensity of the peak at 3.42 eV corresponding to the wurtzite phase was observed to deteriorate faster than that of the peak around 3.1 eV correlated to the cubic phase. This gave rise to an increasing peak intensity ratio (I_C/I_H) for minor cubic to major hexagonal phase with increasing fluence [inset Fig. 2(a)], indicating a possible hexagonal-to-cubic phase transformation in the irradiated NWs.[10]

To remove the defects and finally to examine the realistic nature of the phase transformation in well crystalline NWs, a two-step annealing process was performed for 15 min at 650 °C and 2 min at 1000 °C in N_2 ambient. With the reappearance of the peak around 3.42 eV, RT PL study for the postannealed NWs showed the presence of both peaks with reduced intensity as compared to that for the pristine NWs [Fig. 2(b)]. The positions of the peak corresponding to E_g were shifted toward lower energy (''redshift''). The ''redshift'' of the peak position corresponding to E_g in the postannealed NWs was appreciable for the sample irradiated above a fluence of 1×10^{15} cm^{-2}. However, the ''redshift'' was reduced in the postannealed sample irradiated at a high fluence of 1×10^{16} cm^{-2}. The ''redshift'' was maximum for postannealed NWs irradiated at an optimum fluence of 5×10^{15} cm^{-2}. The peak was shifted to 3.28 eV, which is close to the direct band-to-band transition peak reported for c-GaN phase at RT.[11]

Temperature-dependent CL study of postannealed NWs irradiated at an optimum fluence of 5×10^{15} cm^{-2} showed

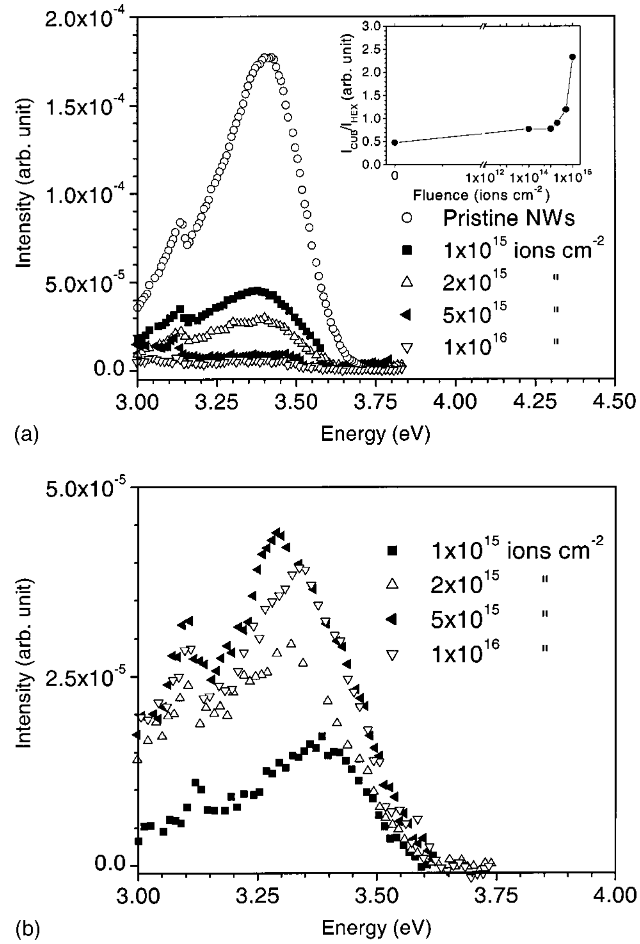

FIG. 2. (a) RT PL spectra for the pristine and as-irradiated NWs showing rapid deterioration of peak corresponding to direct band-to-band transition energy with increasing fluence. Inset shows fluence dependence of peak intensity ratio for the cubic and hexagonal phases. (b) RT PL spectra for the postannealed NWs irradiated with different fluences.

[Fig. 3(a)] an expected ''blueshift'' with decreasing temperature. E_g peaked around 3.25 and 3.3 eV at RT and 4 K, respectively, confirming the presence of cubic phase in the system.[12] Small difference in E_g (RT) in PL and CL measurements fell within the limit of discrepancy reported for the GaN system.[13] The fitting [inset to Fig. 3(a)] of the temperature dependence of peak energies of the band-to-band transition matched well with the reported values of Varshni parameters [$\alpha=6.697\times10^{-4}$, Debye temperature ($\Theta$) of GaN=600 K; $E_g(T)=E_0-\alpha T^2/(T+\Theta)$ where calculated E_g for cubic phase at 0 K (E_0)=3.302 eV] for c-GaN.[12] The defect band around 3.1 eV corresponding to LO phonon replica mode of cubic phase observed in the RT PL studies could not be traced at low temperature CL plots. The asymmetry in the RT-CL plot, however, indicated the presence of peak around 3.1 eV. The comparison of secondary electron and CL (excited at 3.3 eV) images [Fig. 3(b)] at 4 K shows a large number of NWs are in cubic phase.

HRTEM analysis of postannealed NWs always showed h-GaN as major phase with some amount of cubic phase embedded (not shown in picture) in NWs irradiated at a fluence of 2×10^{15} cm^{-2}. Postannealed NWs irradiated at an optimum fluence of 5×10^{15} cm^{-2} showed [Fig. 4(a)] the presence of single cubic phase with zone axis lying along [0 −1 1] direction and lattice parameter was calculated to be 0.455 nm, close to the reported value for c-GaN.[1] The lattice

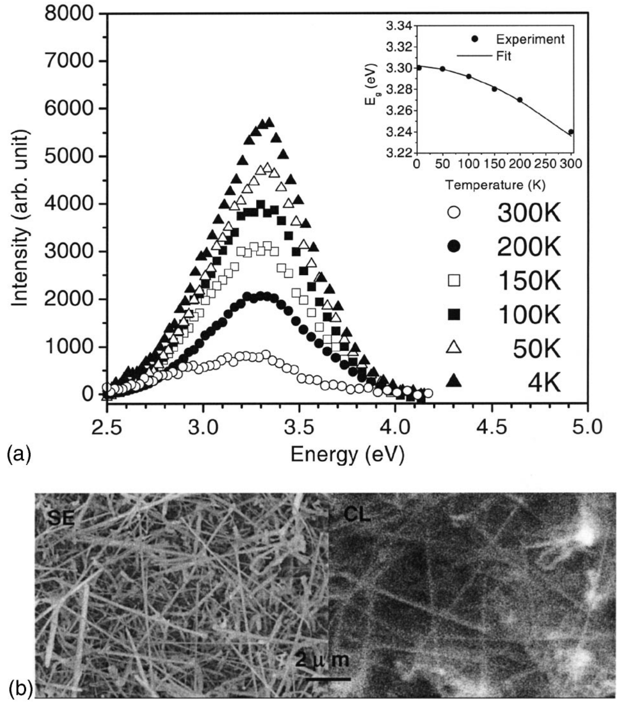

FIG. 3. (a) Temperature dependent CL spectra for the postannealed NWs irradiated with an optimum fluence of 5×10^{15} cm^{-2} showing the presence of cubic GaN. Inset shows the temperature dependence of the band-to-band transition peak energies. (b) SE and CL (excited at 3.3 eV) images at 4 K showing large of the NWs are in cubic phase.

parameter in cubic phase was increased to 0.47 nm for the postannealed NWs irradiated at a fluence of 1×10^{16} cm^{-2} with zone axis lying along [0 0 1] direction [Fig. 4(b)]. The increase in the lattice parameter showed the presence of strain in postannealed NWs irradiated above the optimum fluence causing shift of peak energy corresponding to E_g toward higher energy than that observed for NWs irradiated at an optimum fluence [Fig. 2(b)].

The phase transformation, observed at an optimum fluence of 5×10^{15} cm^{-2}, may be due to sufficient accumulation of Ga from the implanted source in reducing the surface energy and simultaneously stabilizing the cubic phase.[1–3,7]

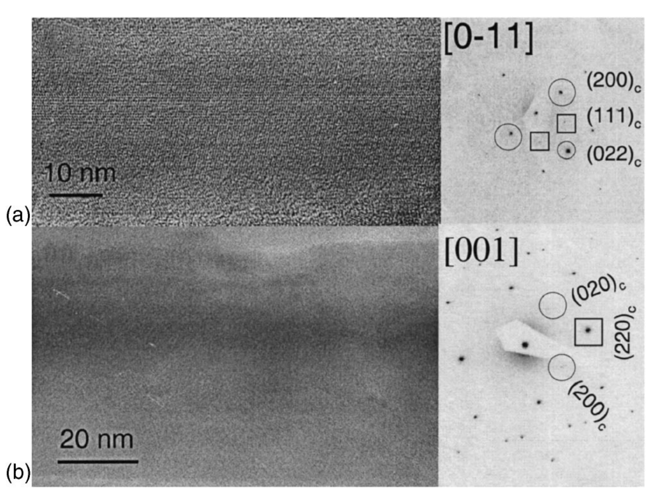

FIG. 4. HRTEM lattice image of the postannealed NW irradiated at fluences of (a) 5×10^{15} cm^{-2} and (b) 1×10^{16} cm^{-2}. Corresponding SAED patterns are shown in the inset, showing the formation of cubic GaN phase with respective zone axes.

Meanwhile, the most likely fluctuations that can lead to nucleation sites for the second phase are those that are short ranged. This is observed in the case of first-order phase transition where the phenomenon occurs discontinuously.[14] We have reported enhanced dynamic annealing (defect annihilation) in as-irradiated GaN NWs with short-range order appearing around an optimum fluence of 5×10^{15} cm^{-2}, as efficient annealing takes place at high diffusivity of mobile point-defects in the high-curvature geometry of NWs.[10] The ''redshift'' observed here for the postannealed NWs irradiated at a fluence of 2×10^{15} cm^{-2} [Fig. 2(b)] implies the presence of minor cubic phase, which may have nucleated at the defect sites with short-range order appearing in as-irradiated NWs around this fluence, showing discontinuous nature of first-order phase transition. ''Redshift'' of peak corresponding to E_g is also reported for GaN sample with mixed cubic and hexagonal phases.[13] All of our evidence for the formation of the cubic phase of the postannealed GaN NWs by HRTEM [Fig. 4(a)], PL [Fig. 2(b)], and CL (Fig. 3) are for the sample irradiated at an optimum fluence of 5×10^{15} cm^{-2}. The phase transition takes place in an inhomogeneous nucleation process where the nucleation starts about particular sites and grows to encompass the whole sample. The nucleated second phase at the defect sites may dominate during recrystallization upon annealing.

In conclusion, a complete hexagonal-to-cubic phase transformation is observed for postannealed GaN NWs irradiated with 50 keV Ga^+ at an optimum fluence of 5×10^{15} cm^{-2}. The exact origin, either Ga playing a role of surfactant reducing the surface energy or the fluctuations in the short-range order induced by enhanced dynamic annealing with the irradiation process, in stabilizing the cubic phase and causing the phase transformation to occur cannot be determined definitely. Nevertheless, the formation of c-GaN NWs, with its various technological advantages over h-GaN, will be useful for futuristic device applications.

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