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Ion-beam-induced reconstruction of amorphous GaN

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Wurtzite GaN can be rendered amorphous by high-dose heavy-ion bombardment. We show here that relatively low-dose reirradiation of such amorphous GaN (*a*-GaN) with MeV light ions can significantly change some of the physical properties of *a*-GaN. In particular, light-ion reirradiation of *a*-GaN results in (i) an increase in material density, (ii) the suppression of complete decomposition during postimplantation annealing, (iii) a significant increase in the values of hardness and Young's modulus, and (iv) an apparent decrease in the absorption of visible light. Transmission electron microscopy shows that *a*-GaN remains completely amorphous after light-ion reirradiation. Therefore, we attribute the above effects of light-ion reirradiation to an ion-beam-induced atomic-level reconstruction of the amorphous phase. Results indicate that *electronic* energy loss of light ions is responsible for the changes in the mechanical properties and for the suppression of thermally induced decomposition of *a*-GaN. However, the changes in the density of *a*-GaN appear to be controlled by the *nuclear* energy loss of light ions.

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High-dose ion implantation is very attractive for several technological steps in the fabrication of GaN-based devices such as selective-area doping and dry etching.[1] However, as reported by several research groups,[2–8] high-dose ion bombardment can render GaN amorphous, which is highly undesirable. Indeed, we have shown that GaN amorphized by heavy-ion bombardment is porous and decomposes during postimplantation annealing at relatively low temperatures (above $\sim 400\,^{\circ}\mathrm{C}$).[6–8] In this Brief Report, we report on a physically and technologically interesting effect where the reirradiation of amorphous GaN (*a*-GaN) with MeV light ions can dramatically change some of its physical properties and, in particular, suppress its thermally induced decomposition. This effect is attributed to an ion-beam-induced atomic-level reconstruction of the amorphous phase. Interestingly, such a reconstruction, resulting in the suppression of material decomposition, is controlled by the excitation of the electronic subsystem of *a*-GaN during light-ion bombardment.

The ~ 2 μm thick wurtzite undoped GaN epilayers used in this study were grown on *c*-plane sapphire substrates by metal-organic chemical vapor deposition in a rotating disk reactor at Ledex Corporation. Continuous surface amorphous layers of different thicknesses were prepared by implantation of GaN with 0.1, 0.3, 0.9, or 2 MeV $^{197}\mathrm{Au}^{+}$ ions at liquid nitrogen temperature using the ANU 1.7 MV tandem accelerator (NEC, 5SDH–4). After amorphization, samples were reirradiated with 600 keV $^{1}\mathrm{H}^{+}$, 1.8 MeV $^{4}\mathrm{He}^{+}$, 1 MeV $^{12}\mathrm{C}^{+}$, 6.6 MeV $^{12}\mathrm{C}^{3+}$, or 2.5 MeV $^{28}\mathrm{Si}^{+}$ ions at room or liquid nitrogen temperature. Before each implantation step, samples were partly masked by a piece of Si so that at the end of the implant sequence each sample had the following areas: (i) as-grown GaN, (ii) GaN as amorphized by Au ion bombardment, and (iii) GaN exposed to both Au and subsequent light-ion bombardment. During implantation, samples were tilted by $\sim 7°$ relative to the incident ion beam to avoid channeling. Postimplantation annealing was carried out in a rapid thermal annealing (RTA) system in a nitrogen ambient at atmospheric pressure.

The surface morphology of implanted as well as annealed samples was studied by tapping mode atomic force microscopy (AFM). The AFM study was performed under ambient conditions with a Nanoscope III scanning probe microscope using commercial single-beam Si cantilevers with force constants of 30–120 $\mathrm{N\,m^{-1}}$. Cross-sectional transmission electron microscopy (XTEM) was performed in a Philips CM12 transmission electron microscope operating at 120 keV. XTEM specimens were prepared by 3 keV Ar^{+} ion-beam thinning using a Gatan precision ion polishing system. As-grown and implanted GaN films were also subjected to room temperature indentation using an ANU UMIS-2000 nanoindentation system with an ~ 4.2 μm radius spherical indenter. The load-unload data were analyzed using the method of Field and Swain[9] to extract the hardness and elastic modulus as a function of indenter penetration.

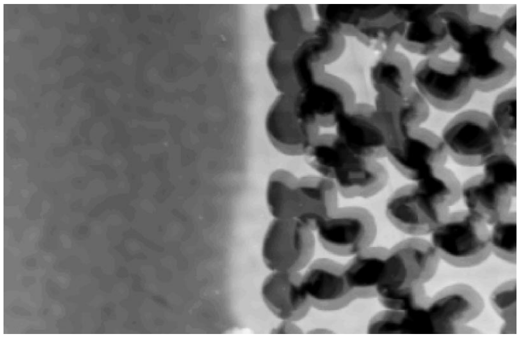

FIG. 1. A top-view height-mode AFM image of a GaN sample amorphized with 2 MeV Au ions implanted at $-196\,^{\circ}\mathrm{C}$ (dose $=1.2\times10^{16}\,\mathrm{cm}^{-2}$, beam flux $=3\times10^{12}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$). After amorphization, one part of this sample (the left half of the image) was reirradiated with 1 MeV C ions at $20\,^{\circ}\mathrm{C}$ (dose$=5\times10^{15}\,\mathrm{cm}^{-2}$, beam flux$=2.5\times10^{12}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$), while the other part of the sample (the right half of the image) was masked. Subsequently, this sample was annealed at $450\,^{\circ}\mathrm{C}$ for 10 min in a nitrogen atmosphere. The horizontal field width of the image is 27 μm.

It should be noted that the main results of light-ion reirradiation reported here are the same for GaN amorphized with Au ions of different energies as well as for *a*-GaN reirradiated with different MeV light ions (^{1}H, ^{4}He, ^{12}C, and ^{28}Si) at room or liquid nitrogen temperature. Below, we illustrate the behavior for the case of light-ion reirradiation of GaN amorphized with 2 MeV Au ions, where the thickness of the resultant surface amorphous layer is the largest as compared to the cases of bombardment with Au ions of lower energies.

Our first observation of light-ion-induced modification of *a*-GaN was a sample color change. Indeed, as-amorphized GaN has a black appearance, while a sample area bombarded with 1.8 MeV He ions during *ex situ* Rutherford backscattering (RBS) analysis[10] is more transparent for visible light than as-amorphized GaN.[11] Thus, light-ion reirradiation appears to reduce absorption of visible light in *a*-GaN. This conclusion is supported by the fact that AFM shows no evidence of light-ion-induced changes in the surface roughness.

As mentioned above, postimplantation annealing of as-amorphized GaN at temperatures above $\sim400\,^{\circ}\mathrm{C}$ results in a complete decomposition of the amorphous layer with the formation of large craters on the surface.[6,8] In Fig. 1, we show a typical AFM image which illustrates such a behavior but also shows the dramatic effect of reirradiation with light ions. After amorphization with heavy ions, one part of this sample (the left half of the image) was reirradiated with light ions, while the other part of the sample (the right half of the image) was masked (see the figure caption for the details of implant conditions). Subsequently, this sample was annealed at $450\,^{\circ}\mathrm{C}$ for 10 min in a nitrogen atmosphere. Figure 1 clearly illustrates that light-ion reirradiation of *a*-GaN effectively suppresses a complete decomposition of the material during postimplantation annealing. Moreover, results show that the formation of craters on the surface of *a*-GaN reirradiated with light ions does not take place during RTA treatment at temperatures up to $1050\,^{\circ}\mathrm{C}$, the maximum annealing temperature used in this study.

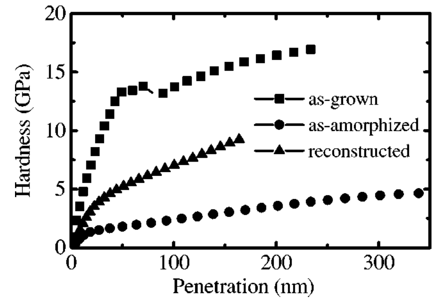

FIG. 2. The curves of hardness as a function of indenter penetration below the circle of contact, as determined from the partial load-unload data. The figure shows data for (i) as-grown GaN, (ii) GaN amorphized with 2 MeV Au ions at $-196\,^{\circ}\mathrm{C}$ (dose$=1.5\times10^{16}\,\mathrm{cm}^{-2}$, beam flux$=5\times10^{12}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$), and (iii) the same *a*-GaN sample reirradiated with 1 MeV C ions at $20\,^{\circ}\mathrm{C}$ (dose$=1\times10^{16}\,\mathrm{cm}^{-2}$, beam flux$=3\times10^{12}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$), as indicated in the legend. The maximum load was 100 mN for as-grown GaN and 40 mN for as-amorphized GaN and *a*-GaN reirradiated with light ions.

Our AFM study also shows that light-ion reirradiation of *a*-GaN increases its density, resulting in a step between as-amorphized and light-ion-reirradiated regions of *a*-GaN.[12] For example, before postimplantation annealing, the step height between as-amorphized and light-ion-reirradiated regions of the *a*-GaN sample shown in Fig. 1 was ~680 Å. This value is less than the step height of ~1570 Å between as-amorphized and unimplanted regions of this sample.[13] Since the amount of *a*-GaN (in atoms/cm^2) does not change during the RBS analysis, this step height change is not due to surface erosion. Therefore, although the average density of light-ion-reirradiated *a*-GaN is much less than the density of as-grown crystalline GaN, light-ion reirradiation somewhat increases the density of *a*-GaN.

Another effect of light-ion reirradiation is illustrated by Fig. 2, which shows the curves of the average contact pressure [or (Meyer) hardness] as a function of indenter penetration below the circle of contact, as determined from the partial load-unload indentation data. This figure shows typical curves for (i) as-grown GaN, (ii) as-amorphized GaN, and (iii) *a*-GaN reirradiated with light ions at room temperature (see implant details in the figure caption). It is seen from Fig. 2 that the value of hardness of as-amorphized GaN is much lower than that of as-grown GaN, which is consistent with a previous report.[14] More interestingly, Fig. 2 illustrates that light-ion reirradiation significantly increases the hardness of *a*-GaN. Table I gives the values of hardness and Young's modulus for as-grown, as-amorphized, and light-ion-

TABLE I. The values of hardness H and Young's modulus E at a plastic penetration depth of 100 nm for the three GaN samples from Fig. 2.

GaN sample	H (GPa)	E (GPa)
as-grown	14.0	233
as-amorphized	2.4	65
light-ion-reirradiated	7.0	99

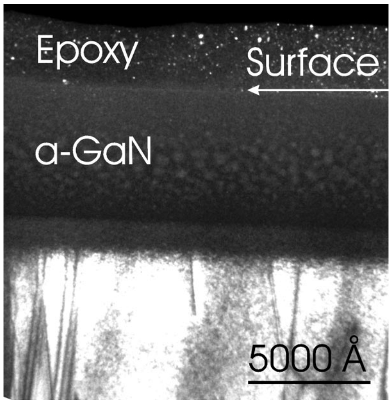

FIG. 3. A dark-field XTEM image (**g**$=$0002*) of GaN amorphized with 2 MeV ions at $-196\,^{\circ}\mathrm{C}$ (dose$=1\times10^{16}\,\mathrm{cm}^{-2}$, beam flux$=5\times10^{12}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$) and subsequently reirradiated with 1 MeV C ions at $20\,^{\circ}\mathrm{C}$ (dose$=5\times10^{15}\,\mathrm{cm}^{-2}$, beam flux$=2.5\times10^{12}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$).

reirradiated GaN (for the three GaN samples from Fig. 2) at a plastic penetration depth of 100 nm.

Such an increase in the values of hardness and Young's modulus as a result of light-ion reirradiation may explain the suppression of material decomposition during postimplantation annealing. Indeed, the catastrophic decomposition of *a*-GaN with the formation of large craters on the surface has been attributed to thermally induced agglomeration of implantation-produced N_2 gas bubbles into larger bubbles with subsequent surface exfoliation.[8] An increase in the values of hardness and Young's modulus of *a*-GaN as a result of reirradiation with light ions is expected to effectively suppress the process of bubble agglomeration and, therefore, subsequent formation of craters.

Finally, Fig. 3 shows a dark-field XTEM image (**g** $=$0002*) of GaN amorphized with 2 MeV Au ions and subsequently reirradiated with light ions. Again, implant details are given in the figure caption. This XTEM image illustrates a surface amorphous layer on the top of a band of implantation-produced defects. The surface amorphous layer in light-ion-reirradiated *a*-GaN (see Fig. 3) has a structure that is very similar to that in as-amorphized GaN (see Refs. 7 and 8) with a high concentration of implantation-produced N_2 gas bubbles. Our detailed XTEM and electron diffraction investigation shows that both as-amorphized and light-ion-reirradiated *a*-GaN samples are completely amorphous. This result indicates that light-ion reirradiation does not result in the (poly)crystallization of *a*-GaN. Therefore, we attribute the above effects of light-ion reirradiation of *a*-GaN to an ion-beam-induced atomic-level reconstruction of the amorphous phase; i.e., to the rearrangement and rebonding of atomic bonds broken during heavy-ion bombardment used to amorphize GaN.

An energetic ion propagating through a solid loses its energy via electronic and nuclear energy loss processes, which can be considered as being independent.[15] Electronic energy loss is due to ion-electron collisions in which the energetic ion excites or ejects electrons of the target atoms, while in a nuclear energy loss process an ion transfers its energy as translatory motion to a target atom as a whole. Electronic

TABLE II. The values of the nuclear (E_n) and electronic (E_e) energy loss of 600 keV H and 2.5 MeV Si ions implanted into GaN.

Ion	E_n (eV Å^{-1})	E_e (eV Å^{-1})
600 keV ^{1}H	9.4×10^{-3}	10.7
2.5 MeV ^{28}Si	8.1	279.4

and nuclear energy loss components can be calculated based on the ion stopping power approach, as is well documented in the literature.[15]

To ascertain whether electronic or nuclear energy loss of light ions is responsible for the light-ion-induced reconstruction of *a*-GaN, we have performed the following experiment. Samples with surface amorphous layers produced by 2 MeV Au ion bombardment were reirradiated at room temperature with 600 keV H ions to doses from 5×10^{15} to $4\times10^{16}\,\mathrm{cm}^{-2}$ or with 2.5 MeV Si ions to doses from 7×10^{12} to $2\times10^{14}\,\mathrm{cm}^{-2}$. Calculations using the TRIM code,[16] a Monte Carlo computer simulation program, show that, for the bombardment of GaN with 600 keV H and 2.5 MeV Si ions, the profiles of the nuclear and electronic energy deposition are essentially uniform throughout the thickness of the surface amorphous layer produced by bombardment with 2 MeV Au ions. Table II gives the values of the nuclear and electronic energy loss for these two implants, as calculated using the TRIM code.[16] From this table, the ratio of electronic to nuclear energy loss is significantly different for these two ions, the ratio being ~1138 for 600 keV H and ~35 for 2.5 MeV Si ions implanted into GaN. Therefore, by analyzing the dose dependence of the effects of light-ion reirradiation of *a*-GaN, it is possible to ascertain whether only nuclear or also electronic energy loss of light ions is responsible for the above effects.

Such an analysis shows that the changes in the mechanical properties and the suppression of thermally induced decomposition of *a*-GaN are controlled by the *electronic* energy loss of light ions. For example, the formation of surface craters during postimplantation annealing of *a*-GaN at $450\,^{\circ}\mathrm{C}$ can be effectively suppressed by reirradiation with 600 keV H ions to a dose of $5\times10^{15}\,\mathrm{cm}^{-2}$ at room temperature, with total nuclear and electronic energy deposition of 4.7×10^{21} and $5.4\times10^{24}\,\mathrm{eV\,cm}^{-3}$, respectively. However, room temperature reirradiation of *a*-GaN with 2.5 MeV Si ions to a dose of $7\times10^{12}\,\mathrm{cm}^{-2}$ (total nuclear and electronic energy deposition is 5.7×10^{21} and $2.0\times10^{23}\,\mathrm{eV\,cm}^{-3}$, respectively) does not suppress thermally induced material decomposition. The total nuclear energy deposition is larger in the case of the Si implant, but the total electronic energy deposition is larger for the H implant. On the contrary, the dose dependence of the step height between as-amorphized and light-ion-reirradiated regions for these two cases of H and Si implants suggests that the changes in material density are controlled by the *nuclear* energy loss of light ions. Indeed, the magnitude of such a step height scales with the nuclear energy deposition and appears to be independent of the electronic energy loss of light ions. Such step height or density changes resulting from nuclear energy deposition are consistent with our previous observations of very large density changes in *a*-GaN caused by bombardment with heavy ions.[7,8]

The above results indicate that the excitation of the electronic subsystem of *a*-GaN is sufficient to induce a rearrangement of atomic bonds broken during amorphization with heavy ions. However, light-ion-induced changes in material density require ballistic processes, which are controlled by the nuclear energy loss of MeV light ions. Therefore, high-dose bombardment of GaN with heavy ions (like ^{197}Au), which generate very dense collision cascades, produces a metastable amorphous phase of GaN that is highly porous. This amorphous phase can be further reconstructed by bombardment with lighter ions, when ion-generated collision cascades are dilute.

The above results show that the density of collision cascades (or the density of nuclear energy deposition), generated by ions in *a*-GaN, plays an important role in controlling material density. This can be attributed to the fact that heavy-ion bombardment of *a*-GaN results in a large decrease in material density due to the effects of ion-beam-induced stoichiometric imbalance and, as a result, material decomposition with the formation of N_2 gas bubbles embedded into a highly N-deficient *a*-GaN matrix. In contrast, in the case of light-ion bombardment, collision cascades are dilute, and the effect of ion-beam-induced stoichiometric imbalance (resulting in large porosity) is much less pronounced compared to the case of bombardment with heavy ions.[17] Hence, the dilute cascades generated by light ions may not further decrease material density but rather have the opposite effect of inducing atomic rearrangements which increase the density part way toward the original GaN density.

In conclusion, light-ion reirradiation of GaN amorphized by heavy-ion bombardment can dramatically change its physical properties and, in particular, suppress decomposition of *a*-GaN during postimplantation annealing. This interesting effect has been attributed to a light-ion-induced atomic-level reconstruction of the amorphous phase. Results indicate that the excitation of the electronic subsystem of *a*-GaN by the ion beam is responsible for such a reconstruction, while the changes in the density of *a*-GaN produced by light-ion reirradiation appear to be due to the nuclear energy loss of light ions.

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[11] Similar changes in the color of *a*-GaN were observed after reirradiation with other MeV light ions, such as ^{1}H, ^{12}C, and ^{28}Si.

[12] Such a step is also present after postimplantation annealing, as can be seen from Fig. 1.

[13] The step height between as-amorphized and unimplanted regions of GaN is a direct consequence of ion-beam-induced porosity and swelling of *a*-GaN. The porous structure of *a*-GaN consists of N_2 gas bubbles embedded into a highly N-deficient *a*-GaN matrix. Such a porosity has been attributed to ion-beam-induced stoichiometric imbalance where N- and Ga-rich regions are produced by ion bombardment. See details in Refs. 7 and 8.

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