Ion-beam-produced damage and its stability in AlN films

S. O. Kucheyev[a)] and J. S. Williams
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

J. Zou
Australian Key Centre for Microscopy and Microanalysis, The University of Sydney, NSW 2006, Australia

C. Jagadish
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

M. Pophristic, S. Guo, and I. T. Ferguson[b)]
EMCORE Corporation, 394 Elizabeth Avenue, Somerset, New Jersey 08873

M. O. Manasreh
Department of Electrical and Computer Engineering, University of New Mexico, Albuquerque, New Mexico 87131

(Received 15 November 2001; accepted for publication 26 June 2002)

Structural characteristics of single-crystal wurtzite AlN epilayers (grown on sapphire substrates) bombarded with 300 keV $^{197}Au^+$ ions at room and liquid-nitrogen temperatures (RT and LN_2) are studied by a combination of Rutherford backscattering/channeling spectrometry and cross-sectional transmission electron microscopy. Results reveal extremely strong dynamic annealing of ion-beam-generated defects in AlN. Lattice amorphization is not observed even for very large doses of keV heavy ions at LN_2. An increase in irradiation temperature from LN_2 to RT has a relatively small effect on the production of stable structural damage in AlN. In contrast to the case of $Al_xGa_{1-x}N$ with $x \leqslant 0.6$, neither damage saturation in the crystal bulk (below the random level) nor preferential surface disordering is revealed for AlN. Results also show that structural lattice disorder produced in AlN by high-dose keV heavy-ion bombardment is stable to rapid thermal annealing at temperatures as high as 1000 °C.
[DOI: 10.1063/1.1501746]

I. INTRODUCTION

In the fast developing field of III-nitride-based (opto)electronics, ion implantation is a very attractive technological tool for several device fabrication steps such as selective-area doping, electrical isolation, dry etching, ion-cut, and quantum-well intermixing.[1] However, in all of these applications, limitations may arise due to ion-beam-produced lattice disorder and its undesirable consequences. Hence, studies of implantation-produced disorder in III nitrides are needed for developing processing technology for III-nitride-based (opto)electronics.

Owing to such technological importance, extensive work has recently been done to understand ion-beam-damage processes in GaN.[1] Implantation-produced lattice damage has also been studied in other III-nitride semiconductors such as AlGaN and InGaN,[2–7] which are used as both active and cladding layers in (opto)electronic devices.[8,9] It has been shown that these group-III-nitride semiconductors exhibit a complex behavior under ion bombardment involving extreme structural changes. In particular, previous studies[1,5–7] have revealed (i) strong dynamic annealing processes (i.e., defect migration and interaction processes *during* ion bombardment) in III-nitrides at liquid-nitrogen temperature (LN_2) and above, leading to the formation of extended defects *during* ion bombardment, (ii) ion-beam-induced porosity and material dissociation, (iii) anomalous surface erosion during bombardment at elevated temperatures, and (iv) preferential surface disordering and layer-by-layer amorphization proceeding from the sample surface. In addition, it has been shown[7] that an increase in Al content strongly enhances dynamic annealing processes, resulting in a suppression in the production of stable lattice disorder in AlGaN under ion bombardment.

Previous studies have shown that disordering in $Al_xGa_{1-x}N$ (with $x \leqslant 0.6$), particularly the profile of structural disorder, is significantly different than that in GaN. Hence, it is important to extend the study to higher Al content, in particular to AlN, to indicate any anomalous disordering behavior that may occur. It should be noted that previous reports on structural characteristics of irradiated AlN have focused on studies of lattice damage produced by bombardment with neutrons or relatively light ions such as 3 MeV Kr ions implanted at room temperature (RT) to a dose[10] of 2×10^{17} cm^{-2} (Ref. 11), 2 MeV Si ions implanted at −195 °C and 127 °C to a dose of 4×10^{16} cm^{-2} (Ref. 12), and neutron bombardment at temperatures from 100 °C up to

[a)]Present address: Lawrence Livermore National Laboratory, Livermore, CA 94550; electronic mail: kucheyev@llnl.gov
[b)]Present address: School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0250.

785 °C.[13,14] It has been shown that, for these implant conditions, AlN does not exhibit amorphization even for relatively large ion/neutron doses [such as ~320 displacements per atom (dpa) for 2×10^{17} cm^{-2} of 3 MeV Kr ions and ~25 dpa for 4×10^{16} cm^{-2} of 2 MeV Si ions in the maximum of the nuclear energy loss profile].[15–17] Previous studies[12–14] have also revealed the formation of an aligned network of extended defects on the basal plane of AlN as a result of irradiation.

However, recent reports[18,19] on ion-beam processes in GaN have shown that, for conditions with strong dynamic annealing (as is the case for AlN at temperatures above, at least, LN_2),[11,12,14] the density of collision cascades (determined by ion mass and energy) may strongly influence the damage accumulation behavior. It has also been shown that the sample surface can act as a nucleation site for amorphization and, hence, dramatically change the damage buildup behavior during ion irradiation.[18,19] Furthermore, chemical effects of implanted species can strongly affect the formation of stable defect structures during dynamic annealing.[19,20] Therefore, in addition to previous structural studies of AlN irradiated with neutrons or MeV (relatively) light ions,[11–14] it is important to investigate damage processes and possible crystalline-to-amorphous phase transformations in AlN under bombardment with keV heavy ions, which produce dense collision cascades close to the sample surface. Such bombardment with keV heavy ions at low temperatures represents an irradiation regime when (i) ion-beam-damage-induced lattice amorphization is most plausible (due to very large density of collision cascades) and (ii) chemical effects of implanted species can be less pronounced in cases of implantation with (relatively) chemically inactive species such as Au.[19]

It should also be noted that all previous studies of irradiation-produced structural lattice damage in AlN have been done on a polycrystalline material analyzed by transmission electron microscopy (TEM).[11–14] However, in order to quantitatively study damage accumulation up to high levels of lattice disorder, other analytical methods, in addition to TEM, should be applied. Rutherford backscattering/channeling (RBS/C) spectrometry is a technique ideally suited to quantitatively study implantation-produced lattice disorder with high depth resolution. However, RBS/C requires a single-crystal material and, hence, has not been applied in previous studies of radiation effects in polycrystalline AlN ceramics.

In this article, we study structural characteristics of single-crystal AlN bombarded with keV heavy ions (300 keV $^{197}Au^{+}$ ions) at RT and LN_2. We study the behavior of damage buildup and the microstructure of ion-beam-produced stable defects in AlN. Results reveal extremely strong dynamic annealing of ion-beam-generated defects in AlN, leading to the situation when lattice amorphization does not occur even for very large doses of keV Au ions at LN_2. Results also show that implantation-produced disorder in AlN is thermally stable up to high temperatures (at least, 1000 °C).

II. EXPERIMENT

About 2000-Å-thick AlN films (with a concentration of Ga impurity of ≲1 at. % introduced during growth, as assessed by RBS) were grown on *c*-plane sapphire substrates by metalorganic chemical vapor deposition in a rotating disk reactor at EMCORE Corp. Samples were implanted with 300 keV $^{197}Au^{+}$ ions at −196 °C or 20 °C with an average scanned beam flux of $\sim3.1\times10^{12}$ cm^{-2} s^{-1} over the dose range from 8×10^{13} to 4×10^{16} cm^{-2} using an ANU 1.7 MV tandem accelerator (NEC, 5SDH-4). Ion irradiation under such conditions created from ~0.46 to ~230 dpa at the maximum of the nuclear energy loss profile.[15] During implantation, samples were tilted by ~7° relative to the incident ion beam to minimize channeling.

After implantation, all samples were characterized *ex situ* at RT by RBS/C using an ANU 1.7 MV tandem accelerator (NEC, 5SDH) with 1.8 MeV $^{4}He^{+}$ ions incident along the [0001] direction and backscattered into a detector at 105° relative to the incident beam direction. This 15° glancing-angle detector geometry was used to provide enhanced depth resolution for examining damage accumulation in relatively thin AlN films and also to separate Au and Al peaks in RBS/C spectra in samples implanted up to high Au doses ($\gtrsim5\times10^{15}$ cm^{-2}). Selected samples were also studied by cross-sectional transmission electron microscopy (XTEM) in a Philips CM12 transmission electron microscope operating at 120 keV. Specimens for XTEM were prepared by 3.5 keV Ar^{+} ion-beam thinning using a Gatan precision ion-polishing system.

III. RESULTS AND DISCUSSION

Figure 1 shows selected RBS/C spectra which illustrate the damage buildup (in the Al sublattice) in AlN films bombarded at −196 °C [Fig. 1(a)] and 20 °C [Fig. 1(b)] with 300 keV Au ions. It is seen from Fig. 1 that, with increasing ion dose for both LN_2 and RT bombardment regimes, implantation-produced lattice disorder accumulates mainly in the crystal bulk (~700 Å from the sample surface), close to the region where the nuclear energy loss profile of 300 keV Au ions is maximum. Interestingly, no preferential surface disordering has been observed in this study in AlN bombarded at either −196 °C or 20 °C.[21] This is consistent with a previous report,[7] showing that the AlGaN surface is not a preferential site for amorphization, in contrast to the situation in GaN.

The damage buildup behavior for heavy-ion bombardment at both −196 °C and 20 °C is better illustrated in Fig. 2, which shows the dose dependence of the RBS/C yield (normalized to the random level) in the bulk defect peak region for AlN samples bombarded with 300 keV Au ions. Figure 2 shows that bulk disorder in AlN gradually increases with increasing ion dose and approaches the random level (suggesting amorphization of the lattice) for ion doses above $\sim2\times10^{16}$ cm^{-2} for both LN_2 and RT bombardment regimes. Interestingly, Fig. 2 shows that an increase in implantation temperature from −196 °C to 20 °C results in only a slight decrease in the level of stable ion-beam-produced lattice disorder. This result is consistent with previous electron

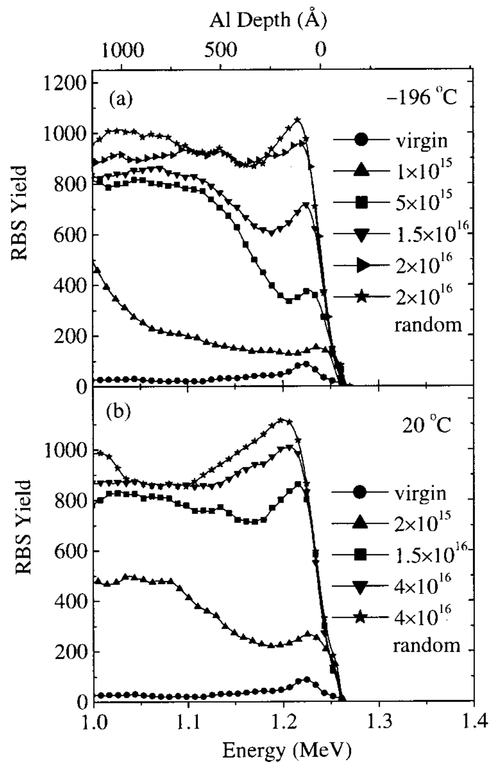

FIG. 1. RBS/C spectra showing the damage buildup for 300 keV Au ion bombardment of AlN at −196 °C (a) and 20 °C (b) with a beam flux of $\sim 3.1\times 10^{12}$ cm^{-2} s^{-1}. Implantation doses (in cm^{-2}) are indicated in the legend. Only the Al part of spectra is shown. Note that random spectra are given for ion doses of 2×10^{16} cm^{-2} (a) and 4×10^{16} cm^{-2} (b).

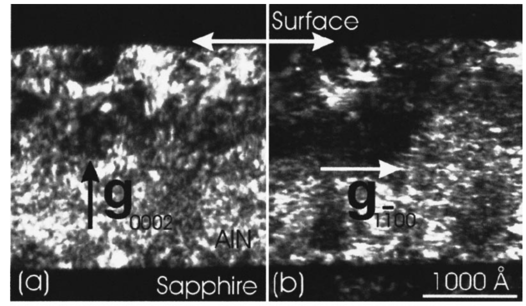

FIG. 3. Dark-field XTEM images [(a) $\mathbf{g}=0002^*$ and (b) $\mathbf{g}=1\bar{1}00^*$] of an AlN epilayer bombarded at 20 °C with 300 keV Au ions with a beam flux of $\sim 3.1\times 10^{12}$ cm^{-2} s^{-1} to a dose of 4×10^{16} cm^{-2}. Images (a) and (b) are of the same magnification.

paramagnetic resonance (EPR) studies of the effect of irradiation temperature on the damage accumulation in AlN bombarded with neutrons,[22] where a very weak irradiation-temperature effect has been observed for temperatures from −248 °C up to −23 °C. Such a weak irradiation-temperature dependence of stable defect formation, revealed in both the present study of structural disorder and a previous report on irradiation-produced paramagnetic centers,[22] suggests that the mobility and annihilation of ion-beam-generated Frenkel pairs in AlN is very large even at −196 °C and does not significantly increase upon increasing sample temperature up to 20 °C. However, as has recently been discussed in detail in Ref. 18, dynamic annealing processes in compound semiconductors may be very complex. At present, more work is needed for a better understanding of complex ion-beam-damage processes (such as defect mobility as well as interaction and annihilation of defects) in AlN.[23–25]

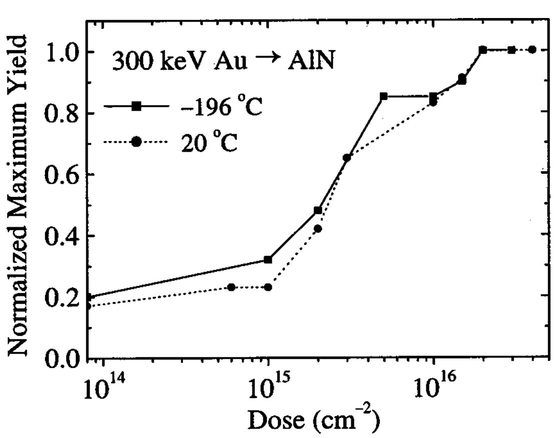

FIG. 2. Dose dependence of the RBS/C yield (normalized to the random level) in the bulk defect peak region for AlN samples bombarded with 300 keV Au ions with a beam flux of $\sim 3.1\times 10^{12}$ cm^{-2} s^{-1} at −196 °C and 20 °C, as indicated in the legend. Lines are shown to guide the reader's eye.

Another interesting feature illustrated in Fig. 2 is that, in contrast to the case of RT heavy-ion bombardment of $Al_xGa_{1-x}N$ with $x \leqslant 0.6$ reported in Ref. 7, Fig. 2 reveals no damage saturation in the crystal bulk at an intermediate (i.e., below the random) level. Indeed, for $Al_xGa_{1-x}N$ with $x \leqslant 0.6$, with increasing ion dose, the level of implantation-produced lattice disorder in the crystal bulk increases up to ~50% and then saturates.[7] During this saturation regime and before a catastrophic collapse of the lattice into an amorphous state, the level of lattice disorder in the $Al_xGa_{1-x}N$ bulk (~50%) is essentially independent of ion dose. Figures 1 and 2 reveal a rather different damage buildup behavior in AlN.

The absence of such damage saturation in AlN suggests that the damage buildup in AlN proceeds via the formation of different types of lattice defects as compared to the case of AlGaN with lower Al content. Hence, in selected samples, the microstructure of implantation-produced disorder has been studied by XTEM. Figure 3 shows dark-field XTEM images of an AlN epilayer implanted at 20 °C with 300 keV Au ions to a dose of 4×10^{16} cm^{-2}. Figure 3 illustrates that, even for a high ion dose when the RBS/C yield reaches the random level in the crystal bulk [see Fig. 1(b)], the AlN layer is heavily damaged but not amorphous.[26] Indeed, no evidence for an amorphous phase has been revealed in this sample by an electron diffraction analysis. This result indicates extremely high radiation resistance of AlN and a large mobility of ion-beam-generated point defects, consistent with previous studies.[5,11,12]

Figure 4 shows the evolution of microstructural changes in AlN bombarded at −196 °C with 300 keV Au ions to different doses. It is seen from Figs. 4(a) and 4(b) that, even for a relatively large dose of 5×10^{15} cm^{-2} of heavy ions, in the near-surface region (up to ~500 Å from the sample surface), where the nuclear energy loss is relatively small, the density of ion-beam-produced defects is low. For larger

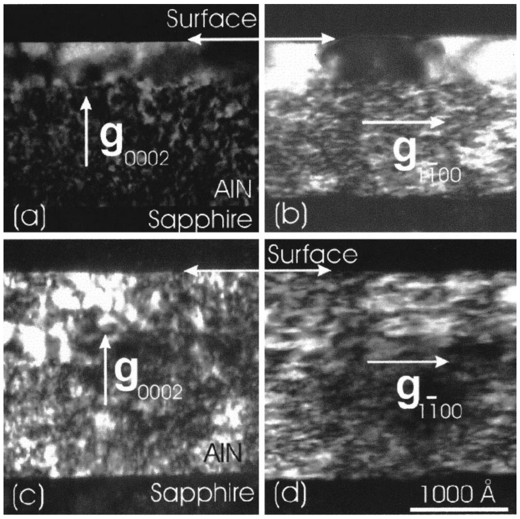

FIG. 4. Dark-field XTEM images [(a), (c) **g**=0002* and (b), (d) **g** =1$\bar{1}$00*] of AlN epilayers bombarded at −196 °C with 300 keV Au ions with a beam flux of ~3.1×10^{12} cm^{-2} s^{-1} to doses of 5×10^{15} cm^{-2} [(a) and (b)] and 3×10^{16} cm^{-2} [(c) and (d)]. All images are of the same magnification.

depths, a dense band of coarse defects can be seen.[27] For the sample bombarded to a larger ion dose of 3×10^{16} cm^{-2}, Figs. 4(c) and 4(d) reveal a dense band of coarse lattice defects throughout the entire AlN film, with no evidence for amorphization. Hence, due to extremely large dynamic annealing processes, it appears to be impossible to induce lattice amorphization in AlN by keV ion bombardment at LN_2 and above.[28]

Finally, our results show that ion-beam-produced lattice disorder in AlN is particularly stable during rapid thermal annealing at temperatures as high as 1000 °C. Indeed, 1 min thermal annealing at 1000 °C (in a nitrogen ambient at atmospheric pressure) of samples bombarded with 300 keV Au ions at either −196 °C or 20 °C to doses $\gtrsim 1\times10^{16}$ cm^{-2} results in a negligible (~5%) reduction in the RBS/C yield, indicating that ion-beam-produced disorder in AlN is not appreciably removed during such annealing. This annealing behavior is not unexpected since the extremely efficient dynamic annealing that occurs in AlN even at LN_2 causes ion-beam-generated Frenkel pairs either to efficiently annihilate or to form stable (energetically favorable) defect structures that accumulate with increasing ion dose. In such a case, one can expect that these complex defect structures will be thermally stable up to high temperatures in AlN. Indeed, as a general rule, temperatures of ~2/3 of the melting point (in K) are required to remove ion-beam-produced extended defects in semiconductors,[1] suggesting that temperatures of $\gtrsim$1900 °C may be needed to anneal out implantation-produced damage in AlN.

It should also be noted that previous studies of the annealing behavior of neutron-irradiated AlN ceramics by optical absorption,[24] EPR,[22,25] and thermal diffusivity measurements[29] have shown that the annealing behavior of irradiated AlN ceramics largely depends on irradiation conditions such as irradiation dose and temperature. For example, in AlN irradiated with neutrons to a relatively low dose of ~1×10^{17} cm^{-2}, defects revealed by EPR and optical absorption measurements[24] show a one-stage annealing behavior at temperatures around ~200 °C, but defects could not be completely removed even by anneals at 500 °C. Moreover, thermal diffusivity and macroscopic length change measurements of AlN irradiated to a larger neutron dose (~2×10^{20} cm^{-2}) have shown that irradiation-produced disorder can not be completely recovered even during 1 h thermal anneals at temperatures as high as ~1400 °C.[29] Hence, previous data also support the aforementioned conclusion that large thermal budgets (with temperatures $\gtrsim$1400 °C) are necessary to completely remove complex defect structures in AlN crystals implanted to high ion doses.

IV. CONCLUSIONS

In conclusion, the structural disorder produced in single-crystal AlN by keV heavy-ion bombardment has been studied by a combination of RBS/C and XTEM. Results show that AlN exhibits extremely strong dynamic annealing of ion-beam-generated defects during ion bombardment at LN_2 and above. In particular, the AlN lattice is not rendered amorphous even for very large doses of keV heavy ions implanted at either −196 °C or 20 °C. Our results have also revealed neither saturation of damage below the random level in the AlN crystal bulk [typical for $Al_xGa_{1-x}N$ with $x \leqslant 0.6$ (Ref. 7)] nor preferential disordering at the AlN surface [typical for GaN (Ref. 1)] for both LN_2 and RT bombardment regimes. This study also shows that implantation-produced lattice defects in AlN are stable up to high temperatures (at least, 1000 °C).

ACKNOWLEDGMENT

This research was supported in part by the Australian Research Council.

[1] See, for example, a recent review by S. O. Kucheyev, J. S. Williams, and S. J. Pearton, Mater. Sci. Eng., R. **33**, 51 (2001), and references therein.
[2] J. C. Zolper, S. J. Pearton, C. R. Abernathy, and C. B. Vartuli, Appl. Phys. Lett. **66**, 3042 (1995).
[3] C. B. Vartuli, S. J. Pearton, C. R. Abernathy, J. D. MacKenzie, and J. C. Zolper, J. Vac. Sci. Technol. B **13**, 2293 (1995).
[4] A. Y. Polyakov, M. Shin, M. Skowronski, R. G. Wilson, D. W. Greve, and S. J. Pearton, Solid-State Electron. **41**, 703 (1997).
[5] J. S. Williams, Mater. Sci. Eng., A **253**, 8 (1998).
[6] S. O. Kucheyev, J. S. Williams, J. Zou, S. J. Pearton, and Y. Nakagawa, Appl. Phys. Lett. **79**, 602 (2001).
[7] S. O. Kucheyev, J. S. Williams, J. Zou, G. Li, C. Jagadish, M. O. Manasreh, M. Pophirstic, S. Guo, and I. T. Ferguson, Appl. Phys. Lett. **80**, 787 (2002).
[8] S. J. Pearton, J. C. Zolper, R. J. Shul, and F. Ren, J. Appl. Phys. **86**, 1 (1999).
[9] S. Nakamura, in *Properties, Processing, and Applications of Gallium Nitride and Related Semiconductors*, edited by J. H. Edgar, S. Strite, I. Akasaki, H. Amano, and C. Wetzel (INSPEC-IEE, London, 1999).
[10] In this article, we are using the term ''ion dose'' (in ions/cm^2) which is well accepted in literature on ion implantation into semiconductors. However, it should be noted that, in literature on irradiation effects in ceramics, ion dose is often referred to as ''integrated ion flux'' or ''ion fluence.''
[11] L. Cartz, F. G. Karioris, and R. A. Fournelle, Radiat. Eff. **54**, 57 (1981).
[12] S. J. Zinkle, L. L. Snead, W. S. Eatherly, J. W. Jones, and D. K. Hensley, Mater. Res. Soc. Symp. Proc. **540**, 305 (1999).
[13] T. Yano and T. Iseki, Philos. Mag. Lett. **62**, 83 (1990).
[14] T. Yano, K. Ichikawa, M. Akiyoshi, and Y. Tachi, J. Nucl. Mater. **283**, 947 (2000).

[15] In the present work, all ballistic calculations of ion-beam-produced atomic displacements have been done with the TRIM code[16] with an effective threshold energy (E_d) for atomic displacements of 25 eV for both Al and N sublattices. It should be noted that we are not aware of any experimental measurements of E_d for AlN. The value of $E_d = 25$ eV, chosen in this work, is close to the value predicted by semi-empirical calculations of Van Vechten.[17] Quoted dpa values are the number of ion-beam-generated lattice vacancies.

[16] J. P. Biersack and L. G. Haggmark, Nucl. Instrum. Methods **A174**, 257 (1980).
[17] J. A. Van Vechten, in *Radiation Effects in Semiconductors*, IOP Conference Series 31, edited by N. B. Urli and J. W. Corbett (Institute of Physics, London, 1977), p. 441.
[18] S. O. Kucheyev, J. S. Williams, C. Jagadish, J. Zou, and G. Li, Phys. Rev. B **62**, 7510 (2000).
[19] S. O. Kucheyev, J. S. Williams, C. Jagadish, J. Zou, G. Li, and A. I. Titov, Phys. Rev. B **64**, 035202 (2001).
[20] S. J. Zinkle and C. Kinoshita, J. Nucl. Mater. **251**, 200 (1997).

[21] It should be noted that a distorted shape of the RBS random spectra from Fig. 1 (i.e., a yield increase near the surface and a dip for larger Al depths) is due to (i) a large concentration of Au atoms implanted into the AlN lattice and (ii) an overlap of Al and Au peaks in the spectra for very large Au ion doses. Note that, for clarity, the Au peak is not shown in Fig. 1.

[22] K. Atobe, M. Okada, and M. Nakagawa, Nucl. Instrum. Methods Phys. Res. B **166**, 57 (2000).

[23] Previous optical absorption and EPR studies of neutron-irradiated AlN ceramics[24,25] have revealed an absorption band at ~370 nm and an EPR center with $g = 2.007 \pm 0.001$ with similar annealing behavior. These EPR and optical absorption centers have tentatively been attributed to (isolated) nitrogen vacancies.[24,25] However, more work is obviously needed to identify the origin of these signals. Indeed, given extremely strong dynamic annealing processes in AlN, the the EPR and optical absorption bands observed in Refs. 24 and 25 more likely arise from defect–impurity complexes rather than from isolated vacancies or interstitials.

[24] K. Atobe, M. Honda, N. Fukuoka, M. Okada, and M. Nakagawa, Jpn. J. Appl. Phys., Part 1 **29**, 150 (1990).
[25] M. Honda, K. Atobe, N. Fukuoka, M. Okada, and M. Nakagawa, Jpn. J. Appl. Phys., Part 2 **29**, L652 (1990).

[26] The fact that the RBS/C yield reaches the random level indicates the presence of a large concentration of lattice defects which effectively suppress ion channeling along the *c* axis of the wurtzite structure of AlN. As it is often the case in ion-implanted semiconductors, such apparent lattice randomization measured by RBS/C does not necessary imply complete disordering or amorphization of the material (i.e., complete loss of long-range order), as clearly illustrated by a comparison of Figs. 1(b) and 3.

[27] It should be noted that, in contrast to the case of previous TEM studies of AlN irradiated with MeV (relatively) light ions or neutrons,[11–14] a detailed XTEM study of defects produced in AlN by high-dose keV heavy-ion bombardment (as shown in Figs. 3 and 4) was not feasible in the present work due to a high density of implantation-produced lattice defects. At present, more work is needed to reveal the atomic structure of defects produced in AlN by ion bombardment.

[28] It should be noted that ion-beam sputtering and chemical effects of implanted species hinder damage buildup and amorphization studies for larger ion doses than the doses used in this study.

[29] T. Yano, H. Miyazaki, and T. Iseki, J. Nucl. Mater. **230**, 74 (1996).