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Citation: Journal of Applied Physics 95, 5487 (2004); doi: 10.1063/1.1707232
View online: http://dx.doi.org/10.1063/1.1707232
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/95/10?ver=pdfcov
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Core-level photoemission and near-edge x-ray absorption fine-structure studies of GaN surface under low-energy ion bombardment

Mladen Petravic, a) Prakash N. K. Deenapanray, b) and Victoria A. Coleman
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

Ki-jeong Kim and Bongsoo Kim
Department of Physics and Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang, Kyungbuk 790-784, Korea

Gang Li
Ledex Corporation, No. 9, Ta-Yio First Street, Ta-Fa Industrial District, Kaohsiung County, Taiwan, Republic of China

(Received 12 January 2004; accepted 23 February 2004)

We have investigated compositional changes on GaN surfaces under low-energy Ar ion bombardment using synchrotron-based high-resolution core-level photoemission measurements and near-edge x-ray absorption fine-structure (NEXAFS) spectroscopy. The low-energy ion bombardment of GaN produces a Ga-rich surface layer which transforms into a metallic Ga layer at higher bombarding energies. At the same time, the photoemission spectra around the N 1s core level reveal the presence of both uncoordinated nitrogen and nitrogen interstitials, which we have analyzed in more detail by x-ray absorption measurements at the N K-edge. We have proposed a mechanism for the relocation and loss of nitrogen during ion bombardment, in agreement with some recent experimental and theoretical studies of defect formation in GaN. We have also demonstrated that photoemission spectroscopy and NEXAFS provide a powerful combination for studying compositional changes and the creation of point defects at GaN surface. © 2004 American Institute of Physics. [DOI: 10.1063/1.1707232]

I. INTRODUCTION

The wide-bandgap semiconductor GaN and related nitride compounds have attracted extreme interest in the last few years due to their new and fascinating physical properties and the variety of possible applications, ranging from laser devices for optical telecommunications to applications in high-efficiency solar cells. 1–3 Research into nitride semiconductors has been limited for many years due to difficulties in growing high-quality epitaxial films and in controlling their electrical properties. 4 Rapid advances in thin-film deposition techniques over the past decade, however, have allowed the growth of high-quality crystals and quantum structures which, in turn, has dramatically improved the optical and electronic performance of nitride semiconductors. 4 They are now regarded as the most promising materials for optoelectronic and photonic applications, and will have a great impact on future technologies in these areas.

One of the key issues in the growth of thin films based on nitride semiconductors is related to methods of surface preparation that determine the final device structure. The commonly used method in preparation of GaN surfaces involves plasma etching with Ar added to the gas mixture in order to increase the physical-to-chemical ratio of the etching mechanism. 1,2,5 Several studies investigating changes in surface composition under different etching schemes have demonstrated an increase in the Ga/N ratio at the surface, 1,5,6–9 which has been attributed to the preferential loss of nitrogen. However, a few studies have provided a quite different picture. For example, no changes in surface stoichiometry were reported for either the Ar ion-milling process 10 or N2 ion bombardment 11 of GaN surfaces.

On the other hand, the production of nitride compounds by nitridation of III–V semiconductors has also been studied extensively during the last few years, mainly because of the lack of lattice-matched substrates for epitaxial growth of thin films based on nitride semiconductors. Several nitridation processes have been proposed, including thermal nitridation using NH3 gas, 12 plasma nitridation, 13 or bombardment with low-energy nitrogen ions. 11

The latter method is also widely used in microelectronics for a range of processing steps, such as dopant implantation, implantation isolation, or dry etching. In all these processes, a range of possible changes in surface composition may degrade the performance of final devices. Therefore, it is quite important from a technological point of view to study changes in surface composition and morphology induced by low-energy ion bombardment.

In this article, we report on several changes, including the formation of metallic Ga and nitrogen interstitials, developed on GaN surfaces under the low-energy Ar bombardment. We have employed both photoemission spectroscopy around N, Ga, and O core levels and near-edge x-ray absorp-
tion fine-structure (NEXAFS) spectroscopy around the N K-edge, using synchrotron radiation, to characterize bombarded surfaces. We have also demonstrated a close correlation between the photoemission measurements of structural changes and corresponding NEXAFS measurements of resonant absorption transitions induced by these changes.

II. EXPERIMENT

The samples used in this study were nominally undoped wurtzite GaN epilayers, 2–4 μm thick and grown on c-plane sapphire substrates by metalorganic chemical vapor deposition. All measurements were performed in a UHV chamber attached to the 2B1 beamline of the Pohang Light Source, which delivers photons in the 12–1200 eV range. The main chamber is equipped with a hemispherical electron analyzer (Gammadata SES 100) for photoemission analysis, while an Ar ion gun for sample bombardment is placed in the pre-chamber.

Samples were bombarded under UHV for 10–35 min with 0.4–2.5 keV Ar ions at an angle of ~45° with respect to the surface normal. The core-level photoemission was measured around Ga 3d, N 1s, and O 1s levels. NEXAFS spectra were recorded in the total electron yield (TEY) mode around the N K-edge at various angles of incidence. The energy scale was calibrated using the C 1s peak at 284.6 eV.

The photoemission spectra were normalized to the photoelectron current of the primary photon beam, measured on an Au grid, and then simulated with several sets of mixed Gaussian–Lorentzian functions with Shirley background subtraction. The raw NEXAFS data were also normalized prior to fitting procedure, first by dividing each raw spectrum by the signal from the Au grid, measured simultaneously with NEXAFS, and then by scaling all spectra to the same edge-jump height (for the definition of the edge jump, see Fig. 7). In our NEXAFS measurements, the broadening of spectra was dominated by the instrumental (monochromator) resolution, thus, we fitted all NEXAFS peaks with pure Gaussian line shapes to simulate resonant transitions to bound final states observed in the near-edge spectra.

III. RESULTS AND DISCUSSION

A. Core-level photoemission measurements

The photoemission spectra for Ga 3d levels, taken by 230-eV photons from two as-grown samples and surfaces bombarded with 0.4-, 1-, and 2.5-keV Ar ions for 15 min., are shown in Fig. 1. All Ga 3d emission curves (solid circles in Fig. 1) were deconvoluted into doublets with a spin–orbit splitting of 0.44 eV and branching ratio of 0.60. To exclude any variation in the binding energy due to the possible bombardment-induced band bending, the zero position of the relative binding energy (BE) scale was taken at the Ga 3d 5/2 position of the bulk component A1.

The Ga 3d emission peak from the as-grown sample was fitted with three doublets originating from either GaN (A1; Ga from GaN), gallium oxynitride (B1; Ga from GaOxN) or gallium oxide (C1; Ga from Ga2O3), with the BE of B1 and C1 shifted towards higher binding energy by 0.35 and 0.77 eV, respectively. We note that these shifts are slightly lower than shifts reported in Ref. 18 (0.5 and 1.1 eV, respectively) which we attribute to the lower oxygen content in the oxynitride and oxide phases in our samples.

The emission from the surface bombarded with 0.4-keV Ar ions requires an additional doublet (D1), shifted by 0.55 eV towards lower BE, to achieve the best fit of the experimental curve (see Fig. 1). We associate this new doublet with the production of uncoordinated Ga atoms under Ar bombardment. In particular, the ion bombardment of GaN surface can cause breaking of Ga–N bonds and the production of Ga atoms bonded to fewer electronegative N atoms in the ion-damaged surface region of GaN. The change in chemical environment of Ga causes a spatial redistribution of valence electrons on the Ga atom, creating more screening of the Ga nucleus and, consequently, a less attractive potential seen by core electrons. As a result, the binding energy for core electrons decreases, which explains the shift in peak position of the doublet D1 in Fig. 1.

At the higher bombardment energy of 1 keV, the peak of D1 shifts even further towards a lower BE (see Fig. 1). This shift indicates further decrease in coordination of Ga atoms, created by the preferential removal of nitrogen at these energies. Removal of additional electronegative N atoms from Ga–N bonds creates less displacement of Ga valence electrons and provides the lower binding energy for Ga core electrons. At the same time, the Ga 3d emission exhibits an additional peak E1, shifted towards a lower BE by 1.44 eV. This peak is even more pronounced in the emission from the surface bombarded by 2.5-keV Ar ions (see Fig. 1). The shift in BE of this new component corresponds to the chemical...
shift from elemental Ga \(^8\) and we attribute the peak E1 to the formation of metallic Ga on the ion-bombardeed sample surface. We note here that a similar component to E1 has been observed previously in the Ga 3d spectrum from a double atomic layer of Ga, i.e., a metallic Ga layer deposited on GaN surface. \(^{19}\)

It is worth pointing out here that the formation of metallic Ga on Ar-bombardeed GaN surfaces was observed previously only after annealing the sample above 623 K, \(^8\) while in our case, the metallic Ga forms during bombardment at room temperature.

The metallic Ga can form on GaN surfaces even at lower bombardment energies if one prolongs the total bombardment time. The time effect is illustrated in Fig. 2 for 0.4-keV Ar bombardment. The photoemission spectrum recorded after bombardment for 15 min exhibits only the peak related to the uncoordinated Ga, represented by the same emission curve D1 as in Fig. 1. However, after an additional 20 min of bombardment (making a total of 35 min), the metallic Ga peak E1 emerges from the emission spectrum at its lower BE side (see Fig. 2).

The presence of peaks B1 and C1 in Figs. 1 and 2 indicates the presence of gallium oxides and oxynitrides on the GaN surface even after the ion bombardment. Indeed, our photoemission spectra exhibit a strong emission from O 1s levels (not shown). It is well known that GaN samples grown by metalorganic chemical vapor deposition may contain a large amount of oxygen. \(^{20}\) In addition, the high reactivity of GaN surface to \(\text{H}_2\text{O}\) \(^{21}\) may also be the source of oxygen contamination on bombarded surfaces, even at the characteristic base pressure during Ar bombardment in our experiments of \(10^{-9}\) Torr.

The corresponding photoemission spectra for N 1s levels, taken by 550-eV photons, are shown in Fig. 3. Two components, A2 and B2, separated by 2.5 eV, can adequately fit the experimental data (open circles in Fig. 3) for as-grown sample. The zero position of the BE scale for N 1s emission was taken at the peak position of component A2. We associate this component with the emission from the bulk GaN phase, while assigning the B2 component to the emission from N 1s core level within the oxynitride phase. The difference in peak position of A2 and B2 of 2.5 eV agrees well with this assignment. \(^{22}\)

The increase of C2-shift with the bombardment energy (0.71 eV for 0.4 keV and 1.0 eV for 2.5 keV), indicates, as in the case of D1-shift from Fig. 1, even lower coordination for N atoms at higher bombardment energies. This process even-
ultimately causes depletion of N atoms from the surface and creation of a Ga-rich surface layer.\footnote{\textsuperscript{5}}

Turning now to the origin of peak D2 in N 1\textit{s} emission from Ar-bombarded GaN, we first note that its shift of 6.7 eV towards the higher BE side remains constant, while its intensity increases slightly with the bombardment energy. Similar shift in N 1\textit{s} emission, observed previously from surfaces of some III–V compound semiconductors, such as GaAs, InAs, or InSb (but not GaN!), bombarded by low-energy N\textsuperscript{2}\textsuperscript{+} ions was attributed to the formation of nitrogen interstitials N\textsubscript{i}, most likely in the form of molecular nitrogen, introduced by the implantation of N ions.\textsuperscript{11} The bombardment and subsequent implantation of N ions into the near-surface region eventually causes recombination to molecular nitrogen as the interstitial N builds up below the surface. These large nitrogen molecules remain trapped below the surface, as the surface nitride layer acts as a diffusion barrier for N\textsubscript{2}.\textsuperscript{11} However, the spectrum from GaN samples shown in Ref. 11 does not exhibit any peak at the D2 position following the N\textsuperscript{2}\textsubscript{+} bombardment.

In the case of Ar bombardment, the formation mechanism of nitrogen interstitials in nitride semiconductors, such as GaN, should be quite different. The simplest mechanism may involve displacement of N atoms from GaN lattice into interstitial positions within the collision cascade caused by Ar ion bombardment. The theoretical studies of defect energy levels of nitrogen in GaN predict the existence of a stable interstitial state of the N–N configuration, known as a (100) split-interstitial.\textsuperscript{24,25} Therefore, interstitial nitrogen represents a stable defect state in GaN that can be formed by ion bombardment. The existence of a D2 component in the emission from N 1\textit{s} core levels, shown in Fig. 3, is in full agreement with this picture, and we associate the peak D2 with the formation of interstitial nitrogen within the surface layer of Ar-bombarded GaN. We will come back to this point in Sec. B, when discussing the NEXAFS measurements.

We finish this section by turning once again to Figs. 1 and 3. It is obvious from these figures that the low-energy Ar bombardment dramatically changes the surface stoichiometry of GaN. In general, the change in the Ga/N ratio can be determined from properly normalized and integrated emission intensities of the Ga 3\textit{d} and N 1\textit{s} core levels. To simplify the normalization procedure for Ga and N spectra taken at different photon energies and with the unknown transmission function of the spectrometer for each element, we have normalized the Ga/N ratios to the ratio determined on the as-grown sample. On such a relative ratio scale, the Ga/N ratio for the as-grown sample would equal 1.

In Fig. 4, we plot the normalized ratio of integrated intensities of Ga 3\textit{d} and N 1\textit{s} emission curves as a function of Ar-beam energy. The Ga/N ratio increases rapidly at lower bombardment energies, indicating the preferential loss of nitrogen from the surface, whereas it exhibits a slower rise at higher bombardment energies, most probably due to the formation of metallic Ga on GaN surface.

**B. NEXAFS measurements**

Turning now to NEXAFS measurements, we first introduce a few basic facts we found relevant for the interpretation of NEXAFS data.

NEXAFS is a nondestructive characterization technique that, in the case of semiconductors, probes the partial density of bound states in the conduction band and the bond orientation of atoms and molecules adsorbed on solid surfaces. The structure of any NEXAFS spectra depends on the x-ray absorption cross section of an atom or molecule, defined as the ratio of the number of electrons excited per unit time and the number of incident photons per unit time and area.\textsuperscript{15}

The absorption cross section contains the dipole matrix term \(|\langle f | e \cdot p | i \rangle|\), where \(|i\rangle\) and \(|f\rangle\) refer to the initial and final states, respectively, \(e\) is the unit polarization vector of incident photons, and \(p\) is the electron linear momentum operator.\textsuperscript{15} The presence of the dipole transition term in the expression for the x-ray absorption implies that all NEXAFS transitions strictly follow the dipole selection rule \(\Delta l = \pm 1\), where \(\Delta l\) is the change of the angular momentum quantum number between the initial and final states. For the transitions around the K-edge, where the initial state is a 1\textit{s} state, the final states must contain the contribution from \(p\) orbitals, for example, in the form of \(s + p_z\) or \(p_x + p_y\).

The dipole matrix element is also responsible for the polarization dependence of NEXAFS spectra. For example, in the case of a hexagonal GaN sample oriented with the surface normal \(\mathbf{n}\) parallel to the \(c\) axis (as in the case of samples used in this work), \(1s \rightarrow p_z\) transitions are forbidden if the electric field \(\mathbf{E}\) of the synchrotron radiation is perpendicular to \(\mathbf{n}\). In this particular case, the condition “\(e\) perpendicular to \(p\)” (\(e \perp p\)) is satisfied and the dipole matrix element is equal to zero. Similarly, \(1s \rightarrow p_{xy}\) transitions are forbidden for \(\mathbf{E}\) parallel to \(\mathbf{n}\).

Further, the NEXAFS intensity of each resonance in a crystal of certain symmetry depends on the angle between \(e\) and \(\mathbf{M}\), where \(\mathbf{M}\) represents the direction of maximum molecular orbital amplitude in the final state.\textsuperscript{15} The polarization dependence of NEXAFS spectra can be determined from spectra recorded at different impact angles of the photon beam, achieved by the simple rotation of sample surface with respect to the beam direction.

A typical NEXAFS spectrum, recorded in the TEY mode around the nitrogen K-edge from an as-grown GaN surface,
is shown in Fig. 5. It has been deconvoluted into a number of Gaussians (G1–G5)\(^1\) to simulate several resonant electron transitions from the N 1\(s\) initial state to the final, low-lying states of \(p\)-symmetry in the conduction band.\(^{16,26}\) We have introduced an additional peak, G1a, between peaks G1 and G2 in our simulation shown in Fig. 4, which was not shown in Ref. 16. The existence of this peak is in agreement with the calculated partial density of N \(p\)-states, showing a double-peak structure around the position G1.\(^{26,27}\)

A strong polarization dependence of NEXAFS spectra is illustrated in Fig. 6\(\text{a}\) for photon impact angles of 90°, 52°, and 28°, measured from the sample surface. Figure 6\(\text{b}\) shows the same NEXAFS curves, but for a smaller energy interval. At 90° impact (normal incidence), the electric field vector of synchrotron radiation is perpendicular to sample normal (\(E_n\)), whereas at the more oblique angles of incidence, there is a component of \(E\) parallel to \(n(E)n\). From the polarization dependence shown in Fig. 6\(\text{b}\), one can identify some of the transitions described in Fig. 5 by the Gaussians G1–G5. For example, the distribution of final states in the \(c\) plane exhibits three well-pronounced peaks (P1, P2, and P3 in Fig. 6\(\text{b}\), described by Gaussians G1, G2, and G3 in Fig. 5), corresponding to 1\(s\) → \(s + p\_z\) transitions involving \(\pi\)-bond states.\(^{26}\) The conduction band states in the \(ab\) plane contribute predominantly to the peaks P2, P4, and P5, corresponding to 1\(s\) → \(p\_x + p\_y\) resonant transitions involving \(\sigma\) bonds.\(^{26}\)

In addition, simulations of NEXAFS spectra from Fig. 6 show only the change in intensity of resonance peaks, whereas the energy position and the width of peaks remains constant for all impact angles. Such behavior is characteristic for hexagonal crystals, in contrast to samples of cubic symmetry, which show no angular dependence for intensities of resonant peaks.\(^{16,28}\)

Finally, in Fig. 7 we show NEXAFS spectra taken from both as-grown and Ar-bombarded samples around the N K-edge. The spectrum from the as-grown sample has been deconvoluted into Gaussian functions in the same way as the spectrum from Fig. 5. Each Gaussian corresponds to a well-known resonant transition from the N 1\(s\) initial state to the...
As the bombarding energy increases, the NEXAFS spectra become broader with less pronounced resonant transitions (see Fig. 7). This is characteristic of the increased amount of bombardment-induced disorder within the surface region of GaN at higher bombardment energies.

Furthermore, two additional peaks appear in ion-bombarded spectra. Keeping the position of original Gaussians at fixed energies, the good fit of spectra from the ion-bombarded samples was possible only by introduction of two Gaussian functions, R1 and R2. For the 1-keV bombardment, R1 is shifted to the lower energy relative to G1 by 2.2 eV, whereas R2 is shifted to higher energy by 0.1 eV. For the 2.5-keV bombardment, the position of R1 and R2 with respect to G1 remains the same within 0.1 eV.

To identify the origin of two resonances R1 and R2 we first note that photons with energies larger than the bandgap are absorbed strongly in semiconductors, generating bound electron–hole pairs. The resulting excitonic states may display themselves as a fine structure in absorption spectrum. A well-known example is a C 1s core exciton in diamond.\textsuperscript{29} However, absorption measurements in a range of bulk semiconductors, such as Si, GaAs, and GaN (including our measurements on GaN), have not revealed any well-resolved discrete excitonic levels.\textsuperscript{17,27,28,29} Consequently, our analysis of resonances in N K-edge NEXAFS will be focused on different point defects introduced into GaN by ion bombardment.

Turning now to the origin of resonance R1, we note that its energy position falls below the nitrogen absorption edge, clearly indicating the location of the final empty states for this resonant transition within the energy gap of GaN. The point defects induced by the ion bombardment that may have some empty states in the bandgap include Ga and N antisites (Ga\textsubscript{N} and N\textsubscript{Ga}, respectively), Ga vacancies (V\textsubscript{Ga}) and N interstitials (N\textsubscript{i}).\textsuperscript{24,30,31} As the final states in observed NEXAFS transitions around the N K-edge must have the contribution of N p states in the conduction band, Ga\textsubscript{N} and V\textsubscript{Ga} defects cannot be observed around the N K-edge. On the other hand, the creation of N\textsubscript{Ga} defects under the ion bombardment is energetically unfavorable as it introduces a strong tensile stress around the N antisite.\textsuperscript{24} This leaves N\textsubscript{i} as the favorable point defect responsible for the NEXAFS resonances below the N absorption edge. The position of R1 is in full agreement with the expected position of empty N\textsubscript{i} states, found to be around 1.4 eV above the valence band maximum.\textsuperscript{31} Assuming the bandgap of 3.5 eV,\textsuperscript{26} that leaves the minimum distance between R1 and G1 of 2.1 eV, in agreement with the value of 2.2 eV found in our NEXAFS experiments.

The most stable N\textsubscript{i} configuration in the wurzite GaN structure is the split-interstitial state in which two N atoms share the same substitutional lattice site.\textsuperscript{24,25} Theoretical calculations predict that this defect introduces two singlet states close to the middle of the band gap.\textsuperscript{24,31} The energy position of the resonance R1 observed in our NEXAFS measurements is close to that prediction, and we associate R1 with transitions of N 1s electrons to the empty p-type states of nitrogen interstitials N\textsubscript{i}, most likely in the form of split-interstitials, introduced by ion bombardment in the energy gap of GaN. This assignment is in full agreement with our photoemission measurements around N 1s core level (see Fig. 3), showing the presence of nitrogen interstitials (peak D2 in Fig. 3) in the ion-bombarded GaN sample. Both D2 and R1 are found in photoemission and NEXAFS spectra, respectively, for the same bombardment conditions and with the intensity increasing with the bombardment energy. Therefore, we associate both of them with the creation of the same point defect N\textsubscript{i} in the ion-bombarded GaN.

Turning now to the resonance peak R2 in our NEXAFS measurements shown in Fig. 7, we note that its energy position is above the N K-edge, indicating resonant transitions from N 1s to the conduction band. The point defects that form empty states in the conduction band include N vacancies (V\textsubscript{N}), Ga interstitials (Ga\textsubscript{i}) or N dangling bonds (N\textsubscript{db}),\textsuperscript{24,30,31} but only the latter, N\textsubscript{db}, can be observed in absorption spectra around the N K-edge. Again, our photoemission measurements shown in Fig. 3 confirm the presence of N\textsubscript{db}-type defects (i.e., uncoordinated nitrogen atoms) at ion-bombarded GaN surfaces. Further, both resonances, C2 in Fig. 3 and R2 in Fig. 7, are found for the same bombardment conditions. Thus, we associate both R2 and C2 with the creation of uncoordinated N at the surface of ion-bombarded GaN.

Our proposition is further supported by a previous NEXAFS study of GaN,\textsuperscript{17} where two additional resonance peaks at energies close to resonances R1 and R2, observed in samples implanted with 70–100-keV O, Mg, or Si ions, have been associated with the formation of nitrogen interstitials N\textsubscript{i}, and N dangling bonds N\textsubscript{db}, respectively.\textsuperscript{17}

However, a recent NEXAFS study of thin amorphous GaN films prepared using an ion-assisted deposition (the evaporation of Ga in the presence of a 0.5-keV nitrogen beam)\textsuperscript{32} has provided an alternative explanation for the resonance R2. The NEXAFS spectrum shown in Ref. 32 is dominated by the low-energy peak at the position of resonance R2. The high-resolution spectrum of this peak\textsuperscript{32} has revealed the complete series of vibrational states characteristic for molecular nitrogen (N\textsubscript{2}).\textsuperscript{33} Thus, it was proposed that this peak is associated with the presence of molecular nitrogen in thin amorphous GaN films, but no explanation was given for the origin of this effect.\textsuperscript{32} A possible mechanism for the N\textsubscript{2} formation may involve the well-known effect of stoichiometric imbalance induced by the ion-beam bombardment,\textsuperscript{34} which may produce an excess number of the heavier matrix element (Ga in the case of GaN matrix) at shallower depth and an enrichment with the lighter matrix element (N in the case of GaN) at the greater depth. Indeed, it has been shown recently that the heavy ion bombardment of GaN produces a highly N-deficient GaN surface with a buried N-enriched layer, probably in form of N\textsubscript{2} gas bubbles.\textsuperscript{35}

We note here that in our earlier report\textsuperscript{36} on formation of nitrogen interstitials in ion-bombarded GaN, the resonance R2 was wrongly located at slightly higher absorption energy.

**IV. CONCLUSION**

In conclusion, our results, shown in Figs. 1–7, support the following mechanism for compositional changes on GaN surfaces under the low-energy Ar bombardment. Impact of
energetic Ar ions breaks the Ga–N bonds on the surface of GaN, causing formation of uncoordinated Ga and N atoms at the surface. Coordination of Ga and N decreases at higher bombardment energies, resulting eventually in a loss of nitrogen from the surface and the formation of a Ga-rich layer. At even higher bombardment energies, or prolonged bombardment time, metallic Ga layer forms on the surface. At the same time, some N is displaced into interstitial positions within the collisional cascade, where it most likely forms split-interstitial defects. This process can be greatly enhanced within the collisional cascade, where it most likely forms a Ga-rich layer.

Our results have also shown that the core-level photo-emission and NEXAFS are complementary techniques that form a powerful combination for studying compositional changes on GaN surfaces and for identifying several point defects created in the near-surface region by ion bombardment.

ACKNOWLEDGMENTS

The authors acknowledge the Australian Government’s Department of Industry, Science and Resources for supporting this work through the Access to Major Research Facilities Program. Measurements at the Pohang Light Source were also supported through the x-ray-particle-beam Nanocharacterization Program by MOST and POSTECH Foundation, Korea. One of the authors (P.N.K.D.) is grateful for the financial support of the Australian Research Council.

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