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# Compositional changes on GaN surfaces under low-energy ion bombardment studied by synchrotron-based spectroscopies

Prakash N. K. Deenapanray

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

M. Petravić

*Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia and Department of Physics, School of Mathematical and Physical Sciences, University of Newcastle, Callaghan NSW 2308, Australia*

K.-J. Kim and B. Kim

*Pohang Light Source, Pohang Accelerator Laboratory, Pohang, Kyungbuk 790-784, Korea*

G. Li

*Ledex Corporation, No. 9, Ta-Yio First St., Ta-Fa Industrial District, Kaohsiung County, Taiwan, Republic of China*

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We have investigated compositional changes on GaN surfaces under Ar-ion bombardment using synchrotron-based high-resolution x-ray photoemission (PES) 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 N  $1s$  core levels reveal the presence of both uncoordinated nitrogen and nitrogen interstitials, which we have analyzed in more details by x-ray absorption measurements at NK edge. We have demonstrated that PES and NEXAFS provide a powerful combination for studying the compositional changes on GaN surfaces. 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 has been proposed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1626792]

The wide band gap semiconductor GaN and the related nitride compounds have attracted extreme interest in the last few years due to their fascinating physical properties and the variety of possible applications in optoelectronics and high temperature microelectronics.<sup>1–3</sup> Rapid advances in thin film deposition techniques over the past decade 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.<sup>4</sup>

The commonly used method in preparation of GaN surfaces involves plasma etching<sup>1,2,5</sup> with Ar added to the gas mixture in order to increase the physical/chemical ratio of the etching mechanism. Several studies, investigating changes in surface composition under different etching schemes, have demonstrated an increase in the Ga/N ratio at the surface,<sup>1,5,6</sup> which has been attributed to the preferential loss of nitrogen. However, a few studies have provided quite different picture. For example, no changes in surface stoichiometry have been reported for both Ar ion-milling process<sup>7</sup> and N<sub>2</sub> ion bombardment<sup>8</sup> of GaN surfaces.

In this letter we report on changes in surface stoichiometry of GaN under the low-energy Ar bombardment. We employed both core-level photoemission spectroscopy (PES) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, using synchrotron radiation, to characterize the bombarded surface. We demonstrate the formation of a Ga-rich surface associated with the formation of metallic Ga and nitrogen interstitials, N<sub>i</sub>.

The samples used were nominally undoped wurtzite

GaN epilayers, 2–4 μm thick and grown by metalorganic chemical vapor deposition. All measurements were performed in an UHV chamber attached to the 2B1 beam line of the Pohang Light Source, equipped with a hemispherical electron analyzer (Gammadata SES 100) for PES and an Ar ion gun for sample bombardment. Samples were bombarded under ultrahigh vacuum 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 the Ga  $3d$ , N  $1s$ , and O  $1s$  levels. NEXAFS spectra were recorded in the total electron yield mode around the NK edge at various angles of incidence. The photoemission spectra were fitted numerically with mixed Gaussian–Lorentzian functions with Shirley background subtraction,<sup>9</sup> while the NEXAFS spectra were fitted with Gaussian functions.<sup>10</sup>

The photoemission spectra for Ga  $3d$  and N  $1s$  levels, taken from both as-grown samples and surfaces bombarded with 0.4 and 2.5 keV Ar ions for 15 min, are shown in Figs. 1 and 2, respectively. All Ga  $3d$  emission curves were deconvoluted into doublets with a spin-orbit splitting of 0.44 eV and branching ratio of 0.60. The zero position of the relative binding energy (BE) scale was taken at the Ga  $3d_{5/2}$  position of the bulk component Al. The Ga  $3d$  emission peak from the as-grown sample is fitted with three doublets originating from GaN [A1; Ga(GaN)], gallium oxynitride [B1; Ga(GaO<sub>x</sub>N<sub>y</sub>)], and gallium oxide [C1; Ga(Ga<sub>x</sub>O<sub>y</sub>)], with the BE of B1 and C1 shifted towards higher binding energy by 0.35 and 0.77 eV, respectively.

The emission from the surface bombarded with 0.4 keV

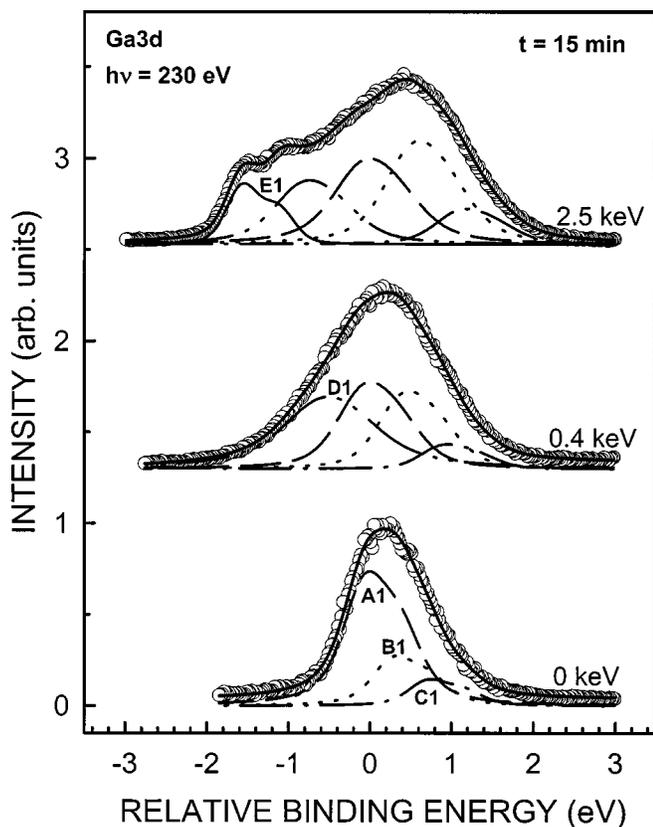


FIG. 1. Photoemission spectra for Ga  $3d$  levels in GaN as a function of Ar ion energy for a sputtering time of 15 min. The solid line is a numerical fit of experimental curve (open circles), representing the superposition of several doublets (A1–E1), each with a spin-orbit splitting of 0.44 eV and branching ratio of 0.60. D1 (uncoordinated Ga) and E1 (metallic Ga) are only observed in ion-bombarded samples.

Ar ions requires an additional doublet (D1), shifted by 0.55 eV towards lower BE. We associate this doublet with the production of uncoordinated Ga atoms (i.e., Ga atoms bonded to fewer electronegative N atoms) in the ion-damaged surface region of GaN.<sup>6</sup> At the higher bombardment energy of 2.5 keV, we note the shift of D1 towards lower BE, indicating a further decrease in coordination of Ga atoms. At the same time, the Ga  $3d$  emission exhibits an additional peak, E1, shifted towards lower BE by 1.44 eV. The shift in BE of this component corresponds to the chemical shift from elemental Ga<sup>6</sup> and we attribute this peak to the formation of metallic Ga on the sample surface.

The corresponding photoemission spectra for N  $1s$  levels are shown in Fig. 2. Two components, A2 and B2, separated by 2.5 eV, can adequately fit the experimental data for as-grown sample. We associate the two components, A2 and B2, to the emission from the bulk GaN phase and the oxynitride phase, respectively.<sup>11</sup>

The emission from sputtered surfaces requires two additional components, C2 and D2, to fit the experimental spectra. Following the same argument as in the case of D1 component of Ga  $3d$  emission, we associate the C2 component of N  $1s$  emission with the breaking of Ga–N bonds under Ar ion bombardment and the formation of uncoordinated N in the damaged surface layer. As expected in this case, the binding energy of Ga- and N-related components shifts in opposite direction reflecting the difference in electronegativity of Ga and N atoms.<sup>12</sup> For higher bombardment energies, C2

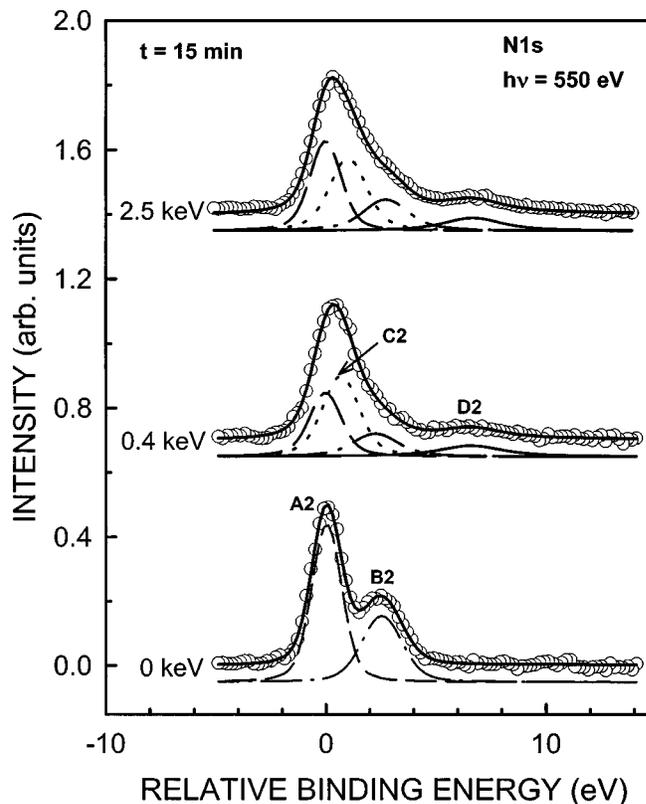


FIG. 2. N  $1s$  photoemission spectra from as-grown and Ar ion-bombarded GaN samples for 15 min. The solid line is a numerical fit of experimental curve (open circles), representing the superposition of several N components (A2–D2). The zero position is taken at the peak of A2.

shifts towards higher BE (0.7 eV for 0.4 keV and 1.0 eV for 2.5 keV), indicating, as in the case of Ga, the reduced coordination of N atoms.

To determine the origin of peak D2 in N  $1s$  emission from Ar-bombarded GaN, we first note that its shift in BE of 6.7 eV towards higher energies remains constant for all bombardment energies. Similar shift in N  $1s$  emission, observed previously from surfaces of InAs and InSb bombarded by low-energy  $N_2^+$  ions<sup>8</sup> was attributed to the formation of nitrogen interstitials,  $N_i$ , most likely in the form of molecular nitrogen.<sup>8</sup> However, in contrast to our study, the spectrum from GaN shown in Ref. 8 does not exhibit any peak at D2 position following  $N_2^+$  bombardment.

The formation mechanism of  $N_i$  in nitride semiconductors, such as GaN, should be quite different. It may involve displacement of N atoms into interstitial positions within the collision cascade caused by Ar ion bombardment, the well-known effect of stoichiometric imbalance induced by ion beam bombardment.<sup>13</sup> The latter may produce an excess number of the heavier matrix element at shallower depth and an enrichment with the lighter matrix element 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  $N_2$  gas bubbles.<sup>14</sup> The theoretical studies of defect energy levels of nitrogen in GaN predict also the existence of a stable interstitial state of the N–N configuration, known as a (100) split-interstitial.<sup>15</sup> Therefore, interstitial, “molecular-like” nitrogen represents a stable defect state in GaN which can be formed by ion bombardment. The existence of D2

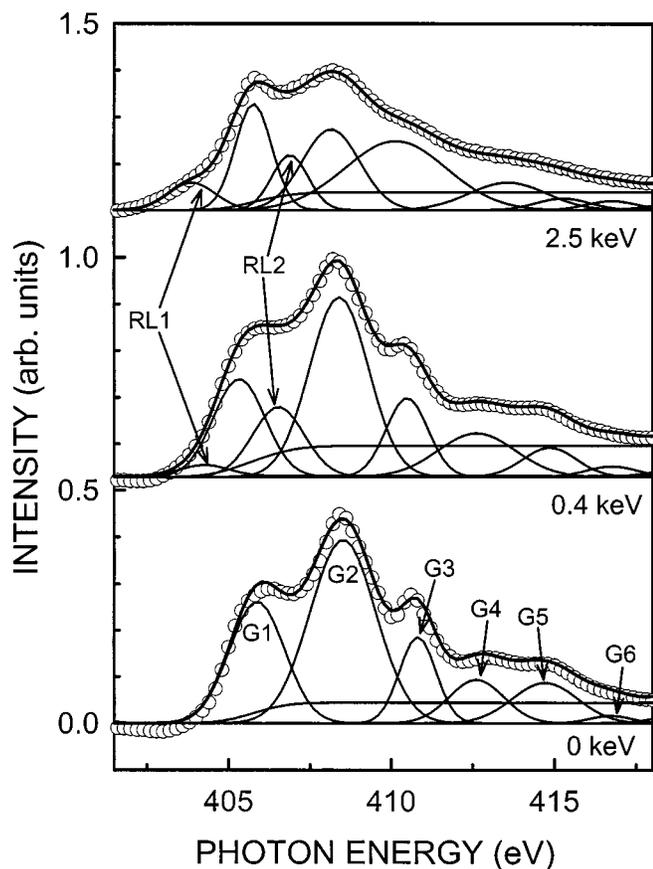


FIG. 3. N K-edge NEXAFS spectra from as-grown and Ar ion bombarded GaN. The spectra were taken at an angle of  $43^\circ$  measured with respect to the surface normal. The solid line is a numerical fit of experimental curve (open circles).

component in the emission from N  $1s$  core levels is in full agreement with the earlier picture and some previous results<sup>8</sup> on III–V compounds and we associate the peak D2 with the formation of interstitial nitrogen.

The further support for such an assignment is provided by NEXAFS measurements taken at the N K edge (Fig. 3). The spectrum from the as-grown sample has been deconvoluted into six Gaussian functions superimposed on a step function, G1–G6 corresponding to well-known resonant transitions from the N  $1s$  initial state to final  $p$  states.<sup>10</sup> As the bombarding energy increases, the NEXAFS spectra become broader with less pronounced resonant transitions, as expected from the increased amount of bombardment-induced disorder within the surface region. Furthermore, two additional Gaussian functions, RL1 and RL2, are required to fit the spectra from the bombarded samples. For the 0.4 keV bombardment, RL1 is shifted to the lower energy by 1.5 eV relative to G1, whereas RL2 is shifted to the higher energy by 1.2 eV relative to G1. For the 2.5 keV bombardment the positions of RL1 and RL2 with respect to G1 are 1.8 and 1.1 eV, respectively. We associate RL1 and RL2 with the formation of nitrogen interstitials,  $N_i$ , and N dangling bonds (i.e., uncoordinated N atoms), respectively, in full agreement with the previous NEXAFS study of ion-implanted GaN.<sup>10</sup>

Turning now to the correlation between our photoemis-

sion and NEXAFS measurements, we first note that an increase of Ar ion energy from 0.4 to 2.5 keV, increases the area under RL1 ( $\sim 9$  times), while, at the same time, the area under RL2 decreases ( $\sim 3.5$  times). Similarly, the normalized area under the peak D2 increases ( $\sim 4.7$  times), whereas the area under the peak C2 decreases ( $\sim 3$  times) when the bombardment energy increases from 0.4 to 2.5 keV (see Fig. 2). The strong correlation between the normalized areas under peaks D2 and RL1 on the one side, and C2 and RL2 on the other, exists over the whole range of ion energies we have studied.

In summary, the results in Figs. 1–3, support the following mechanism for compositional changes on GaN surfaces under the low-energy Ar ion 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 in a loss of nitrogen from the surface and the formation of a Ga-rich layer which, at even higher energies turns into a metallic Ga layer. At the same time, some N is displaced into interstitial positions within the collision cascade. The earlier process can be greatly enhanced and accelerated by the effect of ion-beam-induced stoichiometric imbalance, which may further deplete the surface region of N while, at the same time, it may cause formation of interstitial molecular nitrogen below the surface.

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