Formation of Si clusters in AlGaN: A study of local structure

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In this study, the authors report on the application of synchrotron radiation x-ray microprobe to the study of Si impurities in plasma-induced molecular beam epitaxy grown Al$_{0.32}$Ga$_{0.68}$N. Elemental maps obtained by μ-x-ray fluorescence spectrometry show inhomogeneous distributions of Si, Al, and Ga on the micron scale. X-ray absorption near-edge structure spectra taken at the Si and Al K edges provided information about their local chemical environment and revealed the change of the spectral features as depending on the position compared to the sample surface and on the concentration of Si. © 2007 American Institute of Physics. [DOI: 10.1063/1.2736649]

Blue and UV light emitting diodes and lasers based on AlN and GaN represent important breakthroughs in electronics and optoelectronics. By varying the composition of ternary Al$_{1-x}$Ga$_x$N alloys and by controlled doping, the optical and electrical properties can be tuned over a wide spectral range. Generally, n-type conductivity is obtained by the incorporation of Si, which is supposed to substitute for Ga or Al in the GaN or AlN (Ref. 2) lattice, respectively. However, the dependence of the AlGaN material properties on Si doping is not well understood yet. There are still difficulties in controlling the influence of interstitial dopants, and self-compensation might also affect the doping efficiency. Some reports claim the formation of precipitates by imperfect coalescence, but little information has been gained on them. Thus, the effect of Si on the electronic properties, mechanism of defect formation, alloy disorder, and stress relaxation in AlGaN is still under discussion. In general, the observed strong correlation between electrical and optical properties is explained by a model assuming a random distribution of impurities and defects that may produce local strain and potential fluctuations. Thermodynamical calculations predict no unstable mixing region in ternary AlGaN alloys; thus no phase separation is expected. Nevertheless, recent studies indicated phase separation in Al$_{1-x}$Ga$_x$N films. However, little direct information on the spatial distribution of the alloy composition, impurities, and dopants and their local structure in the AlGaN lattice is available.

We applied synchrotron radiation (SR) excited μ-x-ray fluorescence (XRF) spectrometry to study the compositional homogeneity of Si-doped Al$_{0.32}$Ga$_{0.68}$N films. The hexagonal Ga-face layers were grown on c-plane sapphire by radio frequency plasma-assisted molecular beam epitaxy at ~810 °C substrate temperature using 8 × 10$^{14}$ cm$^{-2}$ s$^{-1}$ total Ga and Al and 10$^{12}$ cm$^{-2}$ s$^{-1}$ Si flux, respectively. The influence of Si incorporation on the local structure of the 1±0.1 μm thick film was investigated by SR-μ-x-ray absorption near-edge structure spectroscopy (XANES). The data were collected at the LUCIA beaml ine of Soleil (SLS, Villigen, Switzerland). The XRF and XANES measurements were performed in vacuum at room temperature at Θ$_0$ =90° ± 1° incident and Θ$_1$ =17° ± 1° detection angles. The XANES measurements in simultaneous fluorescence yield (FLY) and total electron yield (TEY) modes were performed both around the Al (1550–1600 eV) and Si (1830–1890 eV) K edges with 0.2 eV steps. The information depths at the Al/Si K edges in FLY and TEY modes are about 600–700 and ~50–60 nm, respectively.

The compositional homogeneity was investigated by scanning μ-XRF using 1.90 keV excitation energy. Apart from the major elements Al, Ga, and the Si dopant, no additional background impurities were detected in the recent measurement conditions. Elemental maps of Al, Ga, and Si were obtained by measuring their respective $K\alpha$ (Al, Si) and $L\alpha$ (Ga) line intensities in each pixel (Fig. 1). Representative information about the spatial compositional variation was obtained by scanning several areas of $H \times V=0.5 \times 0.2$ mm$^2$. The scans were repeated in smaller areas with high (2 × 1 μm$^2$) spatial resolution. The nonuniform elemental patterns (Fig. 1) indicate compositional inhomogeneity. The relative concentration variations of Al and Ga are ~14% and 30%, respectively. The Si maps show the formation of micrometric (<6 μm) Si-rich clusters having a 20-fold increase of the Si content, anticorrelation between Si and Ga, and colocalization of Si and Al. The Si, Ga, and Al concentrations (Fig. 1) were estimated from the intensities $I_i$ of their characteristic x-ray lines of energy $E_i$, assuming a flat sample, monochromatic incoming beam of $E_0$ energy and $I_0$ flux, and no secondary excitation.
where $k_{i,E_0}$ accounts for the fluorescence yield, detection efficiency, and solid angle, and $C_i$ is the concentration of element $i$. The $p_i$ density of the $d=1$ $\mu$m thick Al$_x$Ga$_{1-x}$N matrix was calculated as $p_i=x_{\text{Al}}\rho_{\text{AlN}}+(1-x_{\text{Al}})\rho_{\text{GaN}}$, where $\rho_{\text{AlN}}=3.23$ g/cm$^3$ and $\rho_{\text{GaN}}=6.15$ g/cm$^3$. The $\mu_i(E)$ mass absorption coefficient is $\mu_i(E) = C_{i0}\mu_0(E)+C_{i\text{GaN}}\mu_{\text{GaN}}(E)$. The $C_{i0}$ was considered to be zero (i.e., 100% Al$_x$Ga$_{1-x}$N), and then it was calculated by taking into account the self-absorption within AlGaN and the $C_{i0}+C_{i\text{GaN}}=100\%$ relation. The lowest and highest Si concentrations are $\approx 0.15\%$ in the cluster-free regions and $\approx 2.8\%$ in the Si-rich clusters, respectively. The average composition of the ternary alloy deduced from the average spectra of the scans is Al$_{0.32}$Ga$_{0.68}$N. Si $K$ edge XANES spectra were measured within and outside the Si-rich clusters in FLY [Fig. 2(a)] and TEY [Fig. 2(b)] modes. The corresponding Si concentrations are indicated in the figures. Al $K$ edge XANES spectra did not vary significantly in different sample points; thus, the average spectra are shown in Fig. 2(d). A XANES spectrum is analogous to the partial density of the empty states of the absorbing atoms and in crystalline material also to the energy band structure. XANES performed at the $K$ edge of a given element (here Si and Al) reveals the $p$-partial density of states in the conduction band. If linearly polarized x-ray beam impinges onto a hexagonal crystal at normal incidence (electric field vector $\perp c$ axis), it probes the 1$a_1$ to $e'_1$ transition, where the $e'_1$ state results from mixing of $p_x$ and $p_y$ orbitals. Thus, in the present experimental arrangement, we used the $p$ conduction band state distribution in the $ab$ plane of the crystal. The significantly different structure of the Al and Si $K$-edge XANES spectra reveals their different local chemical structure. The Al XANES shows remarkable resemblance with the Ga $K$-edge XANES measured in wurtzite-type GaN (Ref. 12) under similar measurement conditions (incident angle of $\approx 90^\circ$). Consequently, Al substitutes for Ga during the crystal growth without significant change of the crystallographic order, suggesting the preservation of the main hexagonal crystal structure. As the Al XANES does not depend on the sample position, the average local chemical environment of Al can be considered to be homogeneous not reflecting the small compositional variation indicated by the $\mu$-XRF maps. The variations of the Si XANES spectra suggest the concentration dependent alteration of the local chemical environment of Si. At the highest Si concentration, the FLY becomes almost structureless with a density of states comparable to that of the continuum, showing the imperfect ordering of Si atoms. The static disorder is larger at the $\approx 60$ nm surface layer indicated by the less intense resonances in the TEY spectra. The spectral characteristics of the FLY spectra (bulk) vary more with the Si concentration than that of the TEY spectra (surface). The significant difference of the TEY and FLY spectra [Fig. 2(c)] shows the modification of the electronic band structure at the surface compared to the bulk. This difference is decreasing with increasing Si content—except peak A (see Fig. 3 for notation), remaining a pronounced feature of the TEY but not of the FLY spectra.

All the Si XANES spectra were fitted by a step function representing the transition of the Si 1$s$ electron to the continuum and by five Gaussians designated by letters A–E in Fig. 3 to simulate transitions to bound final states with $p_{xy}$ component. The energy positions of the edge, peaks A, $B$, and $C$, are independent of the Si concentration both in the TEY and FLY spectra. The constant energy position of the absorption edge indicates no coordination number change within the Si clusters. The energy position, 1846.9 eV, of peak $B$ (transition from Si 1$s$ to $3p_{xy}$ states) suggests the tetrahedral symmetry of the Si atoms. In the FLY spectra (bulk), the intensity of peak $B$ is decreasing while its width is increasing with increasing Si content [Fig. 2(a)]. Consequently, the partial density of unoccupied Si $3p_{xy}$ states is decreasing in the conduction band due to the change of the
crystalline structure/stoichiometry while the local static disorder is increasing (defect formation/partial amorphization). While the intensities of peaks D and E do not show clear dependence on the Si concentration, their energy positions are shifting towards higher energies with increasing Si content, indicating the change of the crystalline structure. The appearance and modification of small XANES spectral features at large $C_{\text{Si}}$ suggest the interaction of the higher neighboring Si tetrahedral orbitals, resulting in molecular orbital overlap forming extended energy bands with modified energies. The increasing Si content increases the disorder leading to amorphous structure.\(^1^3\) At high ($<10^{20} \text{1/cm}^3$) doping concentration, the formation of $\text{Al}_{x}\text{Si}_{1-x}\text{N}$ alloy is suggested in Si-doped AlN.\(^1^4\) A similar process might take place in highly Si-doped AlGaN, which might be indicated by the modified local $C_{\text{Al}}:C_{\text{Ga}}$ ratios found by $\mu$-XRF at high concentration sites of Si. At high enough Si content, the self-compensation of Si by occupying N sites might also appear, which is also suggested by the relatively low free charge carrier concentration ($2.1 \times 10^{18} \text{1/cm}^3$) determined by Hall measurements. These findings are consistent with the observed clustering effects.

In summary, the formation of Si clusters in $\text{Al}_{0.33}\text{Ga}_{0.68}\text{N}$ epitaxial layers was detected by x-ray microprobe. Elemental maps showed compositional modulation—lower Ga and higher Al concentrations—within the Si-rich clusters. Spots of different Si concentrations have been examined around the Si and Al K edges by XANES in FLY and TEY modes. The static disorder around the Si atoms is increasing with increasing Si content, while the hexagonal crystal structure is retained around Al (major component). The difference of the Si TEY and FLY spectra shows its altered local chemical environment/electronic band structure at the sample surface compared to the bulk, which is in agreement with the work of Gao et al.\(^6\) reporting the alteration of the GaAlN composition near the wafer surface. The difference between the Si FLY and TEY spectra is decreasing with increasing Si concentration, where an amorphouslike Si local environment is revealed both at the surface and in the bulk. Although phase separation is considered to be unlikely in AlGaN due to the small lattice mismatch between AlN and GaN, our results indicate its existence. There is no available detailed model for the compositional modulation so far, but it is suggested that different diffusion behaviors of Ga and Al play an important role. Al has much stronger bonding with N and much less mobility compared to Ga. At low $x < 0.5$ Al concentration, the faster Ga diffusion dominates, which facilitates phase separation requiring longer diffusion length. It has been shown for cubic III-V alloys that spontaneous long range ordering compositional modulation is driven by surface and near surface phenomena. So surface kinetic factors might play important roles in such atomic compositional modulation also in AlGaN alloys, which is also strongly influenced by the growth conditions. In the case of metal-rich growth conditions, Si is considered to be a (auto)surfactant both in AlN (Ref. 15) and GaN\(^1^6\) increasing the surface diffusion length of adatoms before being incorporated into an energetically favorable lattice site. Thus, a surfactant-mediated process modifies the site exchange kinetics, determining the growth mode, which might facilitate Si cluster formation.