Strain-induced effects on the electronic structure and N K-edge ELNES of wurtzite AlN and Al\textsubscript{x}Ga\textsubscript{1-x}N

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Abstract. Analysis of the electron energy loss near edge structure (ELNES) provides an experimental tool to probe the density of unoccupied states. Here we present a first principles study on the projected density of states (PDOS) of AlN, GaN, and Al\textsubscript{x}Ga\textsubscript{1-x}N alloys in order to investigate the impact of strain on the N K-edge ELNES. Uni-axial and bi-axial strain, volume conserving, and bi-axial stress deformation modes are calculated for the whole compositional range from AlN to GaN. Our results show that only the strain along the c-axis has a pronounced impact on the PDOS. Furthermore, we find that bi-axial stress in the basal plane, which is present in pseudomorphic polar heteroepitaxial layers, does not significantly influence the N K-edge spectra. However, strain-induced changes may appear for different deformation modes and/or specimen geometries.

1. Introduction

AlN, GaN, and their ternary alloys, Al\textsubscript{x}Ga\textsubscript{1-x}N, are technologically important wide band gap semiconductors used in devices such as light emitting diodes (LEDs) and laser diodes [1]. The large direct band gap of AlN (6.2 eV) makes high Al content Al\textsubscript{x}Ga\textsubscript{1-x}N alloys ideally suited for extending the spectral range of the optoelectronic devices into the deep ultraviolet range. However, due to the substantial lattice mismatch between AlN (\(a = 3.11\) Å, \(c = 4.98\) Å) and GaN (\(a = 3.19\) Å, \(c = 5.11\) Å) [2], residual strain is always present in heteroepitaxial Al\textsubscript{x}Ga\textsubscript{1-x}N structures.

The electron energy loss near edge structure (ELNES), a subset of the electron energy loss spectrum, reflects the density of unoccupied states and thus provides an experimental probe to the electronic structure [3]. The very high spatial resolution that can be achieved in modern transmission electron microscopes, allows e.g. to identify local compositional fluctuations. However, the interaction of the high energy probing electrons with lattice atoms in the specimen does not always have a straightforward interpretation. In order to understand the experimental data, measured EELS spectra need to be compared in detail with their calculated counterparts.

Recently, Keast \textit{et al.} [4] performed an experimental and theoretical study of strain effects in the N K-edge of ELNES in In\textsubscript{x}Ga\textsubscript{1-x}N alloys. In that work, the edge onset was observed to shift towards lower energies with respect to the central peak due to the bi-axial stress. Surprisingly, none of the
numerous papers on experimental and/or theoretical ELNES in AlN, GaN, and AlGaN [5–10] discusses strain effects. In the present work we therefore aim to fill this gap by performing first principle calculations on AlN, GaN and their ternary alloy AlGaN. Strain effects on the unoccupied density of states projected on N-sites for several deformation modes are investigated in order to predict the actual influence on the N K-edge.

2. Methodology
Calculations were carried out within density functional theory (DFT) in the plane-wave pseudopotential approach as implemented in the object-oriented DFT program library S/PHi/nX [11]. Specifically, Troullier-Martin pseudopotentials [12], a plane-wave cut-off of 70 Ry, the Perdew-Berke-Ernzerhof generalised gradient approximation [13] to describe exchange and correlation were used. 576 k-points in the irreducible part of the Brillouin zone were used. An energy convergence of $3 \times 10^{-8}$ eV in the electronic minimisation was employed. Volume relaxation in accord with the deformation modes and relaxation of all atomic coordinates were fully taken into account. Various compositions of the ternary alloy were modelled with $2 \times 2 \times 1$ supercells, where the atoms were distributed according to the special quasi-random structures approach as described in Ref. [14].

The N-K edge ELNES intensity is given by the joint density of the initial and final states. Since the electron is excited from a core N-$s$ state with a very narrow (almost $\delta$-function-like) energy range, the intensity profile is almost exclusively given by the projected density of states (PDOS) for the unoccupied N-$p$ states. Therefore we use the unoccupied N-$p$ PDOS to describe N K-edge ELNES. The calculated PDOS is broadened with a Gaussian having 0.8 eV full width at half maximum.

In order to gather a complete and consistent picture of the effect of strain on the N-$p$ PDOS, several deformation modes were simulated. These were the uni-axial strain along the c-direction ($\varepsilon_{xx} = \varepsilon_{yy} = 0$, $-0.023 < \varepsilon_{zz} < 0.024$), bi-axial strain in the c-plane ($-0.012 < \varepsilon_{xx} = \varepsilon_{yy} < 0.012$, $\varepsilon_{zz} = 0$), deformation with the unit cell volume kept constant ($-0.012 < \varepsilon_{xx} = \varepsilon_{yy} < 0.012, 0.024 > \varepsilon_{zz} > -0.023$), and the bi-axial stress case with $\sigma_{zz} = 0$ ($-0.012 < \varepsilon_{xx} = \varepsilon_{yy} < 0.012, 0.007 > \varepsilon_{zz} > -0.006$) (see figure 1). Here, the uni- and bi-axial strain modes correspond to deformations with assumed Poisson ratio 0. The different deformations were achieved by varying the corresponding lattice parameters. The bi-axial stress mode corresponds to pseudomorphically grown heterostructures. Strain values of the order of 0.01 in the basal plane correspond approximately to pseudomorphically grown layers of Al$_{0.5}$Ga$_{0.5}$N on either GaN or AlN.

![Figure 1](image.png)

**Figure 1.** Deformation modes investigated in this paper: a) uni-axial strain along the c-direction, b) bi-axial strain in the c-plane, c) volume conserving deformations, and d) bi-axial stress with $\sigma_{zz} = 0$. The undeformed unit cells are shown in grey.

3. Results
The evolution of unoccupied N-$p$ states with the amount of aluminium for the constant volume deformation mode is shown in figure 2. On the Al-rich side (figures 2a, b) it is clearly observed that when going from tension ($\varepsilon_{xx} > 0$) to compression ($\varepsilon_{xx} < 0$) in the c-plane, the first (at about 6 eV) and third (at about 11–12 eV) peaks sharpen. Furthermore, the second peak (at about 9–10 eV) diminishes. In contrast, inspecting the Ga-rich side (figures 2d, e) reveals (i) no strain-induced variations of the middle peak, and (ii) a small shift of the position of the third peak at about 11 eV.
Figure 2. Unoccupied broadened N-p PDOS of Al$_{1-x}$Ga$_x$N for the volume conserving deformation mode. Blue solid, black dashed and red dash-dotted lines indicate compressive, zero, and tensile strains in the basal plane, respectively.

Figure 3. Effect of various strain/stress modes on the unoccupied broadened N-p PDOS of AlN: a) uni-axial strain along the c-direction, b) bi-axial strain in the c-plane, c) deformation with constant cell volume, and d) bi-axial stress in the c-plane with $\sigma_{zz} = 0$.

The unoccupied N-p states of AlN for the uni-axial strain along the c-axis and the bi-axial strain in the c-plane deformation modes are depicted in figures 3a and b. An interesting observation is that the middle peak intensity is much more sensitive to the uni-axial than the bi-axial strain case. Figure 3c shows the deformation mode with the constant unit cell volume and reveals the same behaviour as the uni-axial strain case. Based on these results it can be concluded, that it is the deformation along the c-axis which is responsible for the spectral changes in AlN. Lastly, figure 3d suggests that the PDOS variations in the bi-axial stress state are small. This is consistent with fact that for this case deformations along the c-axis are small.

Apart from the strain induced changes in the peak shapes, strain also shifts their positions. The distance between the second and third peaks in the uni-axial deformation mode varies as much as 0.7 eV (2.6 eV for $\varepsilon_{zz} = -0.02$, 1.9 eV for $\varepsilon_{zz} = 0.02$), while the distance between the first and the second peak, as well as the peak distances in the bi-axial strain mode remain almost unaffected. These trends combine in the constant unit cell volume case resulting in a similar behaviour to the uni-axial mode. Finally, in the case of the bi-axial stress deformation, the peak positions remain practically invariant.

4. Discussion

It has been shown that the unoccupied N-p states orientated along the c-axis contribute mainly to the first and third peak of the N K-edge ELNES, whereas the in-plane N-(p$_x$+p$_y$) states contribute to all three peaks [15,16]. This is consistent with our predicted strain response of the N-p PDOS. Deformations along the c-axis (e.g. the uni-axial mode) are expected to influence mainly the p$_z$ states contributing to the first and the third peak. As a consequence, the relative intensities of the three peaks are expected to change. On the other hand, deformations within the c-plane (e.g. the bi-axial
strain mode) affect preferably the \( p_x + p_y \) states. Thus the relative intensities are not expected to vary significantly.

The above described observations have several implications: (i) The second peak in the AlN triplet is highly sensitive to strain along the \( c \)-direction. (ii) Since the physically most relevant strain/stress state for polar (Al,Ga)N material, the bi-axial stress (\( \sigma_{xx} = \sigma_{yy} \neq 0 \) with \( \sigma_z = 0 \) and thus the proper Poisson ratio), shows only a very weak dependence, the experimental N K-edge of Al,Ga\(_{1-x}\)N is expected to be practically strain-independent. (iii) Additionally, the N-K edge onset will also shift depending on the band gap which decreases with the tensile in-plane strain (not discussed here). (iv) When switching from polar to non- and semi-polar materials, which are currently of a great interest, the actual strain-induced changes are predicted to emerge due to different (and much more pronounced) deformations along the \( c \)-axis. To actually observe this effect, much care in the sample design and preparation will be needed as strain will probably be reduced due to relaxation effects resulting from the thinness of the specimen.

5. Conclusions
First principle calculations on strained ternary Al\(_{x}\)Ga\(_{1-x}\)N alloys have been performed with a particular focus on the unoccupied N-\( p \) PDOS as an approximation to the N K-edge ELNES. Our results clearly indicate that applied strain has a substantial effect on peak shape and peak position. These effects are maximised for deformations along the \( c \)-axis. However, significantly less pronounced effects are observed when the in-plane strain is applied in the \( c \)-plane. We explain this behaviour by the fact, that the \( p_z \) states (influenced by the \( c \)-axis deformation) contribute mostly to the first and third peak, while the \( p_x + p_y \) states (affected by the in-plane strain) contribute to all peaks. Finally, we observe that the experimentally obtained bi-axial strain is not likely to influence samples with polar geometry (i.e. when stress is applied along the \( c \)-plane), while it may influence specimens with non- and semi-polar geometries.

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