Analysis of $Al_xGa_{1-x}N$ nanowires through simulated methods of scanning transmission electron microscopy and electron energy-loss spectroscopy

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Abstract

$Al_xGa_{1-x}N$ nanowires have promising applications in ultraviolet light emitting diodes (LEDs). However, these nanowires are not typical p-n junction semiconductors, but rather rely on varying concentrations of Al versus Ga to produce electron hole pairs. More information on the atomic structure is needed to better understand the properties of these nanowires. In this study, $Al_xGa_{1-x}N$ nanowires were imaged using scanning transmission electron microscopy (STEM) and compared to computer simulated STEM images to obtain physical information on the nanowires. Electron energy-loss spectroscopy (EELS) and FEFF9 computer simulations were also performed to better understand the structural and chemical properties of the nanowires. Results from these simulations showed that changes in the chemical ordering of the nanowires were responsible for changes in intensity and resolution in the images. These intensity and resolution trends were not a result of interface effects. This will help to further characterize nanowires in the future.

1. Introduction

Advances in nanotechnology over the past few decades have been driven by a greater understanding of the materials used to create new devices. Electron microscopy provides a means to obtain information necessary to understand structural, chemical and electrical properties of materials. Specifically, the scanning transmission electron microscope (STEM) allows for unprecedented spatial resolution in both heavy and light elements, providing more detailed information on atomic structure.[1] STEM techniques will be used to help obtain physical and chemical information on $Al_xGa_{1-x}N$ nanowires, a new material with applications in ultraviolet light emitting diodes (LEDs). The $Al_xGa_{1-x}N$ nanowires examined are grown in coordination with Ohio State University via Professor S.D. Carnevale. Each nanowire is graded in composition from x = 0 to x = 1 and back to x = 0 with a quantum well of primarily GaN in the center. This produces Ga rich regions at the ends of the nanowires and Al rich regions surrounding the quantum well as shown in Fig. 1. The change in composition from Al to Ga produces electron hole separation, creating a p-n junction without the need of a dopant material as found in traditional semiconducting materials.[2]

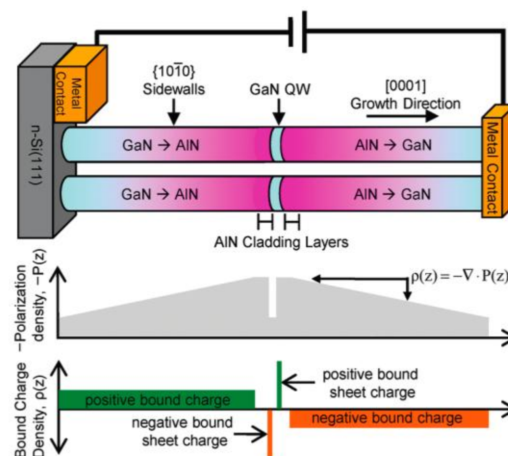

Figure 1: Schematic of $Al_xGa_{1-x}N$ nanowire structure, emphasizing graded compositional change and effect on charge distribution[2]

STEM provides information about a specimen on the atomic scale. Electrons are accelerated from a source, such as cold field or LaB_6, towards the specimen. These electrons are focused prior to reaching the specimen by magnetic coils that alter the electric and magnetic fields that the incident electrons travel through. The electrons converge on the specimen and then scatter through the specimen. Two different detectors are placed below the specimen to obtain a signal: a high angle annular dark field (HAADF) detector and an annular bright field (ABF) detector. HAADF imaging collects electrons scattered at high angles from the central beam and provides good z-contrast images. ABF imaging collects electrons that are scattered at low angles to the central beam and is useful in imaging lighter elements.[3] In using the HAADF and ABF detectors, nanowire images can give information on the composition and structure by observing nitrogen contrast and resolution as well as intensity changes from the atoms. These details help describe what the composition of a specific region of the nanowire might be.

In order to verify the composition, simulated imaging techniques are needed. Simulated STEM images are obtained by using the code developed by Professor E.J. Kirkland at Cornell University.[4] This method involves dividing a continuous specimen into discrete atomic layers. Each layer has a different group of atoms with a certain atomic potential energy associated with the slice. The code calculates the transmission wave function as it passes through each individual layer. Most crystalline materials are sliced in repeating units according to the stacking sequence of the material. However, as the crystals produced have more complicated structures, each layer must be generated individually instead of repeating layers through a sample.[4]

In addition to STEM imaging, electron energy-loss spectroscopy (EELS) also helps characterize atomic scale structures. This technique allows for better understanding of chemical and electrical properties of materials by bombarding the specimen with monoenergetic electrons.

These incident electrons interact with the specimen and collide inelastically with the specimen electrons, causing the incident electrons to lose energy. This lost energy is directly dependent on the material that the incident electrons travel through. The energy value changes as the specimen's composition changes from one element to another. This characteristic energy value can be recorded as a function of the number of incident electrons losing that energy, known as an EEL spectrum. In an EEL spectrum, elemental regions are differentiated by their energy peaks and the overall shape of the spectra.[5]

A useful tool to verify EELS data is a real space multiple scattering code called FEFF9. Similar to the Kirkland code, FEFF9 is a simulation technique that calculates the atomic potentials of a specimen. The phase shifts of the incident electrons are also calculated based on the specimen matrix and energy losses are calculated and quantified. For each of these scattered paths, relative amplitudes are calculated and the simulated EELS spectra are created.[6]

This report focuses simulating STEM images and EELS through the Kirkland code and FEFF9 simulations. Representative crystals based on the gradation of the nanowires are constructed and used for the simulations. The simulated and experimental results are compared to see whether or not the simulations accurately predict the structural and chemical properties of the nanowires. This will help in the future to characterize the composition of Al and Ga along each layer of atoms in the nanowires and verify the target growth of the nanowires.

2. Experimental Procedures

2.1 STEM Imaging and EELS

All STEM imaging was performed on a JEOL JEM-ARM 200CF with a cold field emission gun (CFEG) operated at 200 kV. The electron probe had spherical aberration correctors to allow for spatial resolution down to approximately 65 pm. Four detectors were used with the microscope: high and low angle annular dark field (HA/LAADF), annular bright field (ABF) and

a Gatan EELS system. Imaging was performed with a convergence angle of 22 mrad and a probe current of 10.5 pA.

STEM images were taken of single, isolated nanowires. These nanowires were tilted to a low index zone axis to avoid imaging artifacts. HAADF, LAADF and ABF images were taken of the nanowires near the top and bottom of the samples and at the edge of the quantum well. The HAADF inner detection angle was set to 90 mrad, giving ABF an inner detection angle of 11 mrad, or half of the convergence angle. EELS data were also taken at six different points in the nanowire to show spectra at different Al versus Ga concentrations.

2.2 Kirkland and FEFF9

Simulated STEM images were created using the Kirkland code discussed in Section 1. The Kirkland code required the position of each atom in the specimen being imaged. This was done by creating models of the nanowires using Crystal Maker software. Pure GaN, pure AlN, a single graded structure and a double graded structure were the samples created for simulated STEM, as shown in Fig. 2. The two pure samples were created to verify pure regions in the nanowires and the two graded structures were created to model the nanowire itself. The single graded structure varied in composition along the imaging direction and the double graded structure varied in composition along the imaging direction and along the imaging face. All atomic positions for each of the samples were then recorded into a script file to be entered into the Kirkland code. The Kirkland code also required basic STEM probe parameters and thermal vibration amplitudes of the atoms which were matched to real STEM imaging conditions. Each sample was imaged 15 times from the front face of the sample at intervals of 1 nm and imaged again at the back face of the specimen. HAADF and ABF images were taken at each thickness interval.

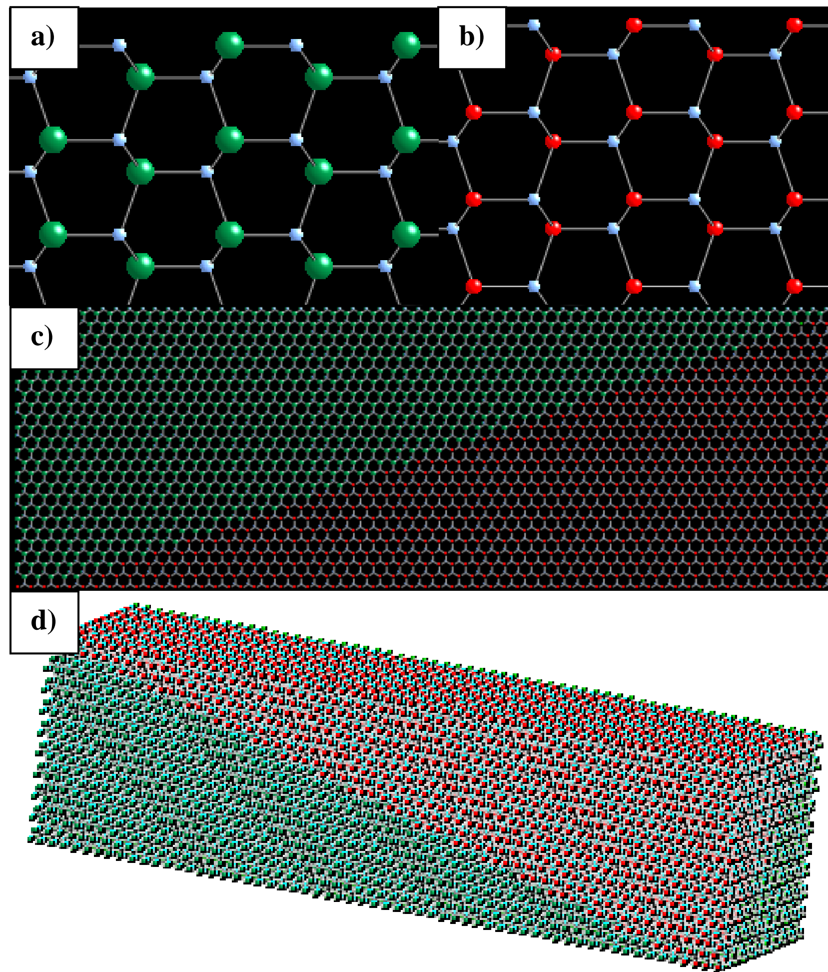

Figure 2: Computer generated crystals created to find atom positions for Kirkland code. All Ga atoms are green, Al atoms red and N atoms blue; a) Pure GaN; b) Pure AlN; c) Single graded structure; d) Double Graded structure

FEFF9 simulations were performed in addition to performing EELS as a comparison to the experimental data. The ATOMS program developed by Professor Bruce Ravel at the University of Chicago was used to obtain the input file necessary to run the FEFF9 program. This input file contained the atoms used, their positions, space group, lattice parameters, and other imaging parameters. Pure GaN and pure AlN were simulated from one shell to ten shells of atoms to show convergence in the calculations. The polarization direction was set to [100] for each sample.

3. Results and Discussion

3.1 Structural Characterization

The Kirkland code, when finished, created HAADF and ABF images at 15 different thicknesses through the simulated nanowires. In Fig. 3, the N of the pure GaN sample is not visible in the HAADF image. However, the N in the pure AlN sample in Fig. 4 is visible in the HAADF image. Both ABF images show N, but the AlN has a better resolution of the N atoms. This is caused by the Z dependence on the intensity in STEM images.[7] Since $Z_{Ga} = 31$ and $Z_N = 7$, the Ga intensity dominates the image in GaN. In the AlN sample, $Z_{Al} = 13$ so the Al and N do not dominate the intensity and both atoms are visible. In addition, the Ga sites in Fig. 3 are larger than the Al sites in Fig. 4, showing the change in size between the two atoms.

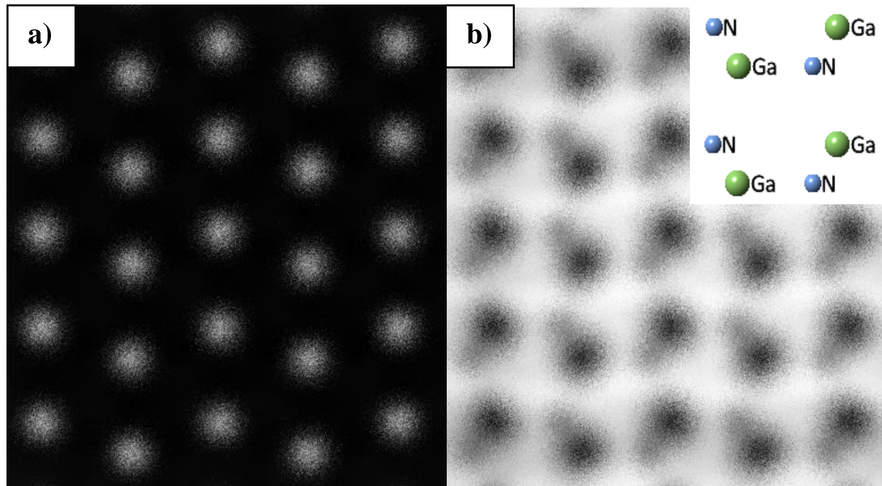

Figure 3: Pure GaN simulated STEM images; a) HAADF; b) ABF

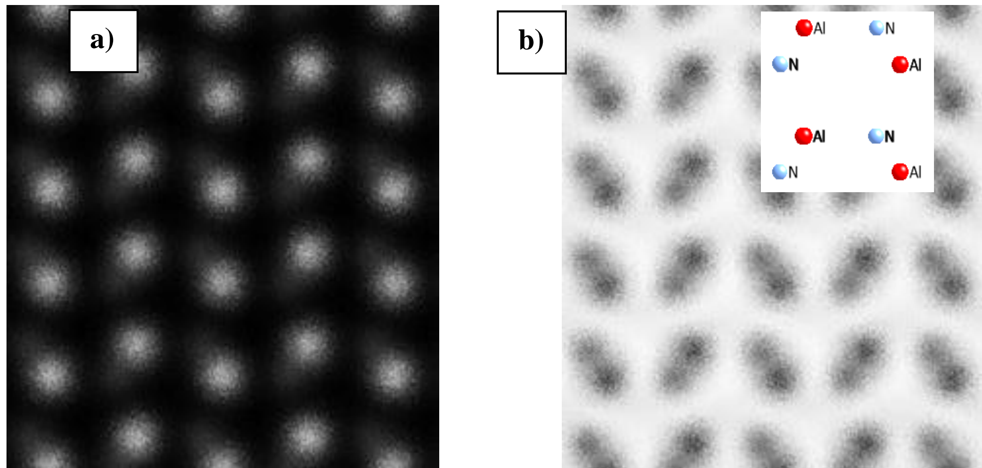

Figure 4: Pure AlN simulated STEM images; a) HAADF; b) ABF

Simulated STEM images of the single graded structure also show the change in intensity between Al regions and Ga regions. In Fig. 5, the composition in both images changes gradually from Ga rich on the left to Al rich on the right. In the HAADF image, the Al rich side has less intense Ga/Al sites than the Ga rich side, showing a clear change in intensity as the composition changes. In the ABF image, the N sites become clearer towards the Al rich side and the Ga/Al sites become smaller towards the Al rich side.

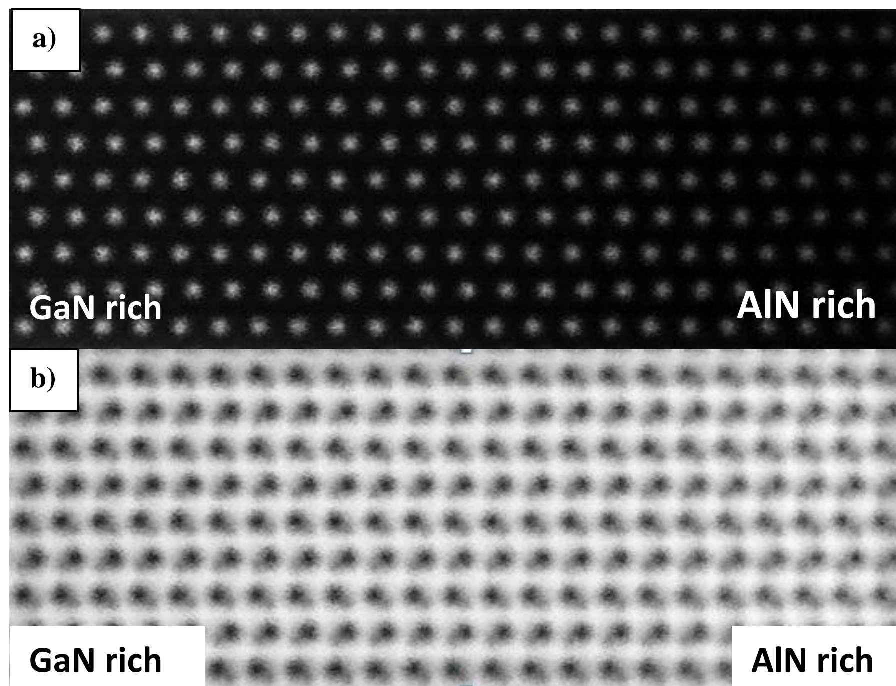

Figure 5: Simulated STEM images of single graded structure 15 nm into the sample; a) HAADF; b) ABF

Simulated STEM images of the double graded structure helped confirm the trends shown in the previous three structures. In Fig. 6, the Al rich region for each image is the top left corner and the composition changes both horizontally and vertically towards the Ga rich region in the bottom right corner. The HAADF image shows more intense Ga/Al sites on the Ga rich side and less intense Ga/Al sites on the Al rich side. The N sites are more distinct in the ABF image on the Al rich side and the size of the Ga/Al sites gets smaller towards the Al rich side. The changes in both the HAADF and ABF images occur moving across a row and up a column, showing the varying composition in both directions.

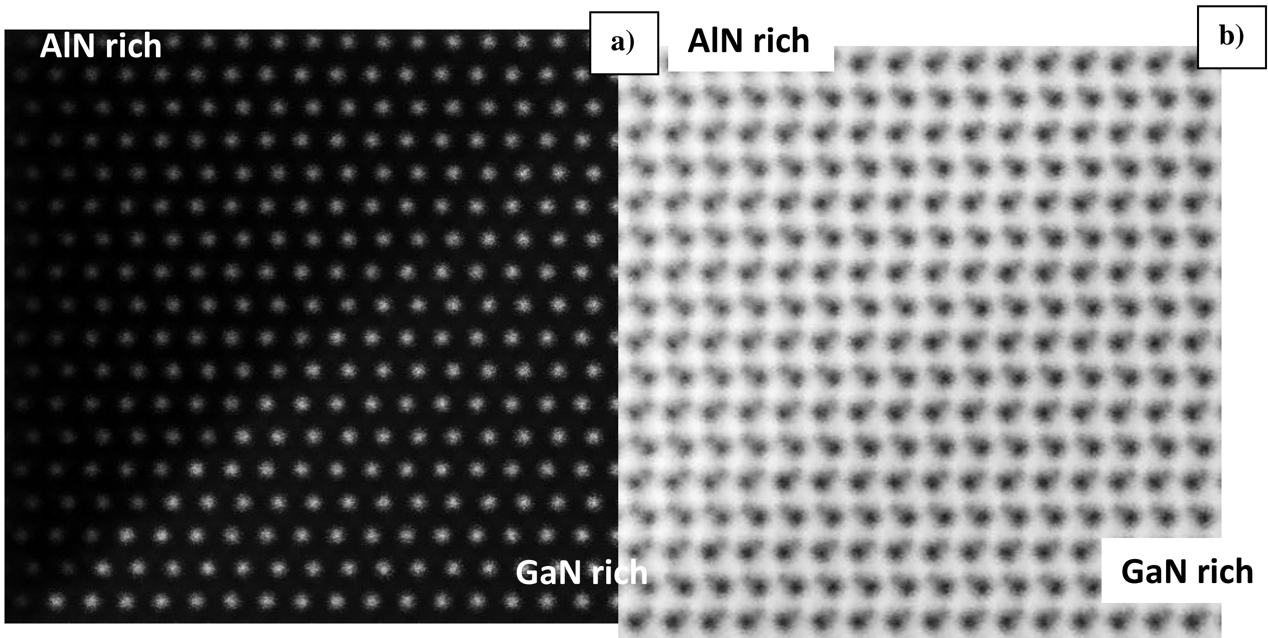

Figure 6: Simulated STEM image of double graded crystal 15 nm into the sample; a) HAADF; b) ABF

All of the trends discussed in the four simulated images match the trends observed in the experimental STEM images. Fig. 7 shows a STEM image in the quantum well region of one of the nanowires. The quantum well is composed of primarily GaN and the region above the quantum well is primarily AlN. As seen in the previous simulated samples, N contrast and

resolution is higher in the Al rich region. The Ga rich region is more intense overall than the Al rich region and the Ga sites are larger than the Al sites.

In order to obtain a better representation of the nanowires, new structures need to be built. These simulated structures should follow the composition of the nanowires: Ga rich on the end to Al rich in the middle surrounding a Ga rich quantum well. This will hopefully give a better line by line view of what the atoms in the nanowire look like under STEM and help confirm that the growth of the nanowires accurately follow the model in Fig. 1.

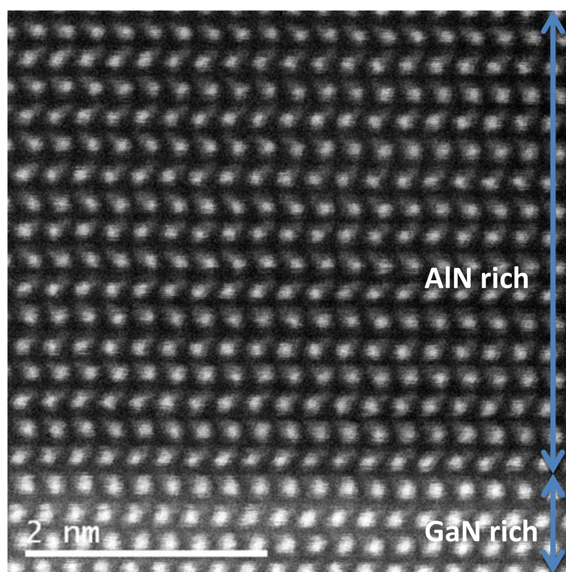

Figure 7: Experiment STEM HAADF image near quantum well displaying separation of Al-rich and Ga-rich areas

3.2 Chemical Characterization

EEL spectra were taken from six different locations within the nanowire shown in Fig. 8. Each site has a different Al and Ga concentration as seen by the change in intensity in the HAADF image of the nanowire. The singular peak shown in the first spectrum, a Ga-rich site, and the three peaks in the third spectrum, an Al-rich site, match previous EELS data taken from similar $Al_xGa_{1-x}N$ samples. [8] This confirms the overall shape of the spectra.

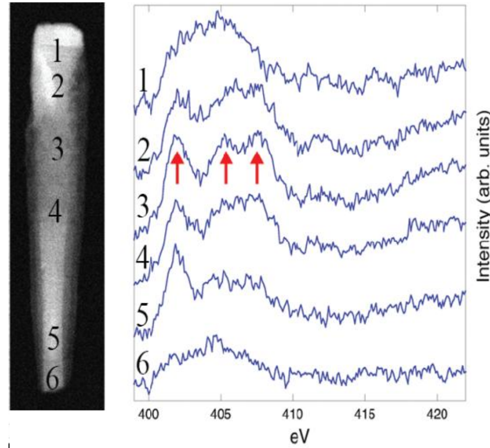

Figure 8: EEL spectra at different locations within the nanowire with an HAADF image of the nanowire labelled at the six spectral points

The FEFF9 code resulted in ten different spectra for both pure GaN and pure AlN, from the first shell to the tenth shell for each sample. The GaN sample converged after the seventh shell and the AlN sample converged after the sixth shell. Fig. 9 shows the two samples after the tenth shell, where the AlN sample is shifted vertically for viewing purposes. In comparison to the experimental results, the AlN sample looks very similar. The three dominant peaks at about 401, 405, and 408 eV respectively match the three peaks shown in the third spectra in Fig. 8. The drop off after these peaks also remains consistent with experiment. The GaN sample has two peaks, one at about 402 eV and one at about 404 eV. This, however, is not consistent with experiment which showed one broad peak in the first spectra in Fig. 8. The plateau after the larger peak in the simulated spectra is consistent with the rest of the experimental spectra.

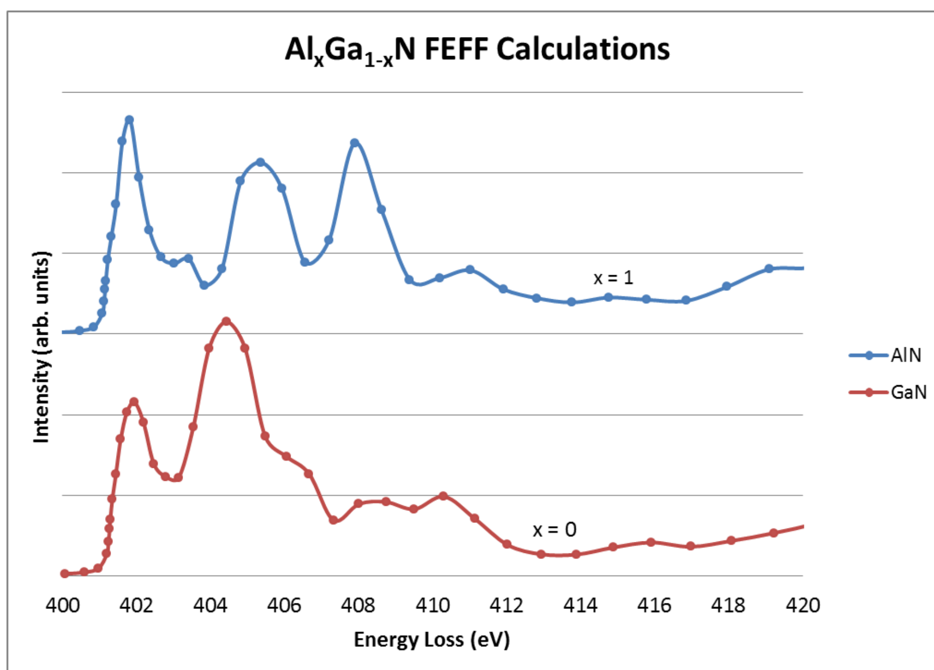

Figure 9: FEFF9 results for pure GaN and pure AlN calculated at the tenth shell

The main issues that arose from performing the FEFF9 simulations were controlling the parameters required in the input file. The shell range values that control the number of shells taken into account for electron scattering were set to the shell number and the shell number plus about 0.7 (10.0 and 10.7 for the tenth shell), but changing these range of values may provide different spectra results. In addition, the number of atoms used in each shell was larger than that used in another experiment at the University of Washington, which could mean that the defined shells are not matched exactly to prior experiments.[6] These factors should be taken into consideration for future experiments.

4. Conclusion

In the simulated STEM images, N contrast was clearer in the Al rich regions and the N atoms had a higher resolution. Al sites were also less intense and smaller in size than the Ga sites. In the FEFF9 simulations, pure AlN spectra showed similar trends to experimental data, having three distinct peaks and leveling off after these peaks. The pure GaN spectra however showed a

secondary peak that was unexpected, while the rest of the spectra matched experimental data. Overall, the simulated results showed that changes in the chemical ordering of the nanowires were responsible for changes in intensity and resolution in the images. These intensity and resolution trends were not simply a result of interface effects within the nanowires.

Future work will begin with graded structures for FEFF9 simulations to obtain spectra at varying Al and Ga concentrations. This will be useful in comparing to experimental EEL spectra in which the composition at the spectral points is unknown. In addition, the input parameters of FEFF9 will be experimented with to find the best results. Finally, more STEM images and EELS data will be obtained and the simulated data found will help characterize the nanowires structurally and chemically. This data will help to verify the target growth of the nanowires.

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