First-principles Calculation of $L_3$ X-ray Absorption Near Edge Structures (XANES) and Electron Energy Loss Near Edge Structures (ELNES) of GaN and InN Polymorphs

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First principles calculations of $L_3$ XANES/ELNES of GaN and InN with both wurtzite and zinc-blende structures have been made using OLCAO (orthogonalized linear combinations of atomic orbitals) method. Supercells with more than 100 atoms were employed. A core-hole was rigorously included in the calculation, and the photo absorption cross section (PACS) between the initial and final states was computed. Quantitative reproduction of experimental spectrum that is available in literature can be found when the PACS was computed. Although spectral shapes of two phases look similar, characteristic differences are predicted to appear at the first peak of the $L_3$ XANES/ELNES. The first peak is notably broader in the zinc-blende phases. The origin of the broadness is analyzed using partial density of unoccupied states (PDOS) and Mulliken charge. We then conclude that the broadness can be related to greater covalency of the zinc-blende phase as compared to the wurtzite phase.

(Received January 26, 2004; Accepted April 8, 2004)

Keywords: X-ray absorption near edge structures (XANES), electron energy loss near edge structures (ELNES), first principles calculation, GaN, and InN

1. Introduction

Electron energy loss near edge structures (ELNES) can be measured with an electron energy loss spectrometer (EELS) which is attached to a modern transmission electron microscopy (TEM). Because ELNES is measured with TEM or scanning TEM (STEM), a spectrum from a few nano or sub-nano areas can be obtained.1) X-ray absorption near edge structures (XANES) measured with X-ray source provides identical information to that of ELNES measured in the transmission mode. Combining a highly sensitive multielements solid state detector (SSD) with synchrotron source, XANES can be obtained from ultra-dilute dopants of a few ppm level with sufficient signal to noise ratio.2) Both ELNES and XANES reflect an electronic transition from a core orbital to unoccupied bands, thereby providing information about atomic and electronic structures around an objective atom.3,4) In order to interpret the spectral features of XANES or ELNES and transfer the information to that of the chemical environments, good theoretical tools that can reproduce the spectra are indispensable. Recently, some of theoretical studies succeeded in quantitative reproduction of the experimental spectra.5–8) In those theoretical studies, three conditions have been commonly fulfilled: 1) An electronic hole at a core-orbital which is accompanied with the electron transition process, i.e., a core hole, has been taken into account. 2) A sufficiently large supercell composed of approximately one hundred atoms has been employed to minimize the effect of core-holes in adjacent cells. 3) Photo absorption cross section (PACS) which is proportional to the electronic transition probability has been computed as a theoretical spectrum. However, the relationship between spectral features and the chemical information has not been discussed in details, even when experimental spectra were well reproduced by the calculations.

Recently, we have revealed the relationship between covalency and spectral shape of Al-$L_{2,3}$ ELNES in wurtzite (w) and zinc-blende (zb)-AlN polymorphs.9) We have emphasized that polymorphs are good models to find such relationships, because the same set of atoms is arranged with different crystal structures. The spectral differences among polymorphs have been successfully ascribed to the difference of electronic structures that is caused by the structural difference. In this study, we applied the same strategy to GaN and InN polymorphs. Wurtzite and zinc-blende is stable and meta-stable phase of both compounds, respectively. Only stacking sequence of close packed planes is different between two phases. The wurtzite structure has AB stacking known as 2H structure, whereas the zinc-blende structure has ABC stacking, i.e. 3C structure. The other difference is the point symmetry of the GaN$_4$ or InN$_4$ structural units. The units in the zinc-blende structure have $T_d$ (tetrahedral) symmetry which is a higher symmetric structure than that of the wurtzite with tetrahedrons of $C_{4v}$ symmetry. In this study, we firstly demonstrate quantitative agreement of experimental Ga-$L_3$ edge spectrum of w-GaN by the theoretical calculation. Then the origins of the spectral differences between the wurtzite and zinc-blende phases is pursued from the viewpoint of chemical bondings using partial density of unoccupied states and Mulliken charges as guides.

2. Procedure

In order to interpret XANES/ELNES, first principles orthogonalized linear combinations of atomic orbitals (OLCAO) calculation has been performed. The OLCAO method is a density-functional theory-based all-electron
method. Each atomic orbital is expressed as a sum of Gaussian-type orbitals. Full basis function sets, i.e., 1s to 5p for Ga, 1s to 6p for In, and 1s to 3p for N, were employed unless otherwise stated. Core-orbitals can be eliminated from the final secular equation by an orthogonalization process, which can significantly reduce a computational time. The details of the OLCAO method have been described elsewhere.\(^ {10}\)

In the ELNES/XANES calculation, it is well known that inclusion of a core-hole which is accompanied with the electron transition from a core-orbital to unoccupied bands is indispensable. In order to introduce the core-hole in the OLCAO method, only the core orbital of the core-hole atom is excluded from the orthogonalized process. When the core-hole is introduced in the periodic-boundary system, use of a large supercell is mandatory in order to minimize the interactions among the core-holes in the adjacent cells.\(^ {5,9}\)\(^ {5,9}\)

In this study, 108 and 128 atoms supercells were employed for wurtzite and zinc-blende structure, respectively. Using such supercells, distance among the core-holed atoms in adjacent cells can be kept to be approximately 1 nm. Both the final and the ground states were separately calculated. Theoretical transition energy was evaluated by the subtraction of the total energy at the ground state from that at the final state. PACS which is proportional to the transition matrix from a core orbital at the ground state and unoccupied bands at the final state was calculated as a theoretical spectrum.\(^ {5} \) Since large supercells were employed in the calculations, only one k-point in the Brillouin zone was used in the self-consistent calculations. In the PACS calculation, eight k-points were adopted to achieve high resolution. We have been using the OLCAO method to calculate XANES/ELNES of many systems and confirmed the usefulness.\(^ {2,5,6,9,11–14}\)

3. Results and Discussion

The experimental and calculated L\(_3\) XANES are shown in Fig. 1. Experimental spectrum has been reported only for w-GaN.\(^ {15}\) Neither ELNES nor XANES of other compounds have not been reported with authors’ best knowledge. In the calculated spectra, each PACS was broadened with Gaussian function of FWHM (full width at half maximum) = 1.0 eV in order to compare with the experimental spectrum. As can be seen in the figure, experimental spectrum of w-GaN is well reproduced by the present calculation. Calculated spectra of the zinc-blende phases are shown below that of the wurtzite phases. The spectra of the zinc-blende phases exhibit numerous similarities with that of the wurtzite phases. The characteristic differences between two phases can be most clearly seen around the peak A. Generally speaking, peak A for the zinc-blende phase is broader than that for the wurtzite phase. The magnitude of the spectral difference is larger in GaN than that in InN. As mentioned above, the unit tetrahedra in the zinc-blende structure shows higher order symmetry than that of the wurtzite structure. Therefore, one could expect smaller number of peaks in the spectrum of the zinc-blende phase. However, the real spectral shape around peak A is opposite to the intuition. The reason can be discussed with the aid of unoccupied partial density of state (PDOS) at the final state as shown in Fig. 2 and Fig. 3.

PDOS are shown together with PACS in Fig. 2 and Fig. 3. In order to interpret the origin of the each peak in a simple manner, the minimal basis function sets, i.e., 1s to 4d for Ga, 1s to 5d for In, and 1s to 2p for N, were employed for both PACS and PDOS calculations. The FWHM of the PDOS and PACS in Fig. 2 and Fig. 3 is taken to be a half of that in Fig. 1 to analyze their structures with high resolution. The lines s, p, and d represent the sum of s-type, p-type, and d-type orbitals, respectively. s+d denotes a simple sum of s and d-PDOS. Following the electric dipole selection rule, only s and d-P DOS play roles for the L\(_3\) spectra.

The shape of PACS is markedly different from that of s+d PDOS. This implies that not only the azimuthal distribution but also radial distribution of the final state wave functions are important for determining the spectral shape. It should also be emphasized that PACS calculation is mandatory for qualitative reproduction of experimental XANES/ELNES.

The difference in spectral shape between wurtzite and zinc-blende has been analyzed for AlN and SiC in our previous

![Fig. 1 Experimental and theoretical XANES/ELNES of w- and zb-GaN(left) and InN(right). Experimental spectrum of w-GaN were reported by Chiou et al.\(^ {15}\) Theoretical spectrum were broadening by Gaussian function with FWHM=1.0 eV.](image1)

![Fig. 2 PACS and unoccupied s, p, d, and the sum of s and d partial density of states (PDOS) at the final state of w-GaN (left) and zb-GaN (right). Employed FWHM of Gaussian function is 0.5 eV. Dashed lines highlight the position of the lowest s and d orbitals.](image2)
study.\textsuperscript{9) }We have reported that the width of the peak A is broader in both GaN and InN. The conclusion seems to be general for covalency between the wurtzite and zinc-blende phases of some different from that of L\textsubscript{3} spectrum of AlN, we found that the same discussion can be made in the present systems. The p+d hybridization is greater in the zinc-blende phases. This can be confirmed by comparing the position of the lowest s and d orbitals which are indicated by dashed lines in both figures. It can be noted that the energy difference between the lowest s and d orbitals in the zinc-blende phases is smaller than that in the wurtzite phases by 0.7 eV for GaN (Fig. 2) and 0.3 eV for InN (Fig. 3). In other words, the lowest d orbital is more stabilized in the zinc-blende structure due to the stronger p+d hybridization. The stronger p+d hybridization makes the d-band broader in the zinc-blende phase as compared with the wurtzite phase, which should be the reason for the broadening of the peak A.

The idea can be well confirmed by the Mulliken’s population analysis as shown in Table 1. The net charges in zinc-blende phases are always smaller than that in wurtzite phases. This means cation-anion bonds are more covalent in zinc-blende phases, which is consistent to the above discussion. It is therefore concluded that the spectral difference in L\textsubscript{3} XANES/ELNES reflects the difference of the covalency between the wurtzite and zinc-blende phases of both GaN and InN. The conclusion seems to be general for these kinds of compounds which is composed of tetrahedrons centered by a cation.

4. Summary

In this work, we have performed first-principles calculations of L\textsubscript{3} XANES/ELNES of GaN and InN polymorphs using the OLCAO method. The theoretical spectra obtained using supercells composed of more than one hundred atoms were able to reproduce the Ga-L\textsubscript{3} XANES of w-GaN quantitatively. Spectral differences in L\textsubscript{3} XANES between the wurtzite and zinc-blende phases were predicted to appear most clearly at the peak A. The peak A of the zinc-blende phases was broader than that of wurtzite phases. Results of the PDOS and Mulliken’s population analysis showed that the shape of the first peak is related to the covalency of the compounds.

Acknowledgements

TM is supported as a JSPS research fellow. This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas (No. 751) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

**REFERENCES**


**Table 1** Net charge of cation in each compound with wurtzite and zinc-blende structures as evaluated by Mulliken’s population analysis by separate minimal basis-set calculations.

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<th>Wurtzite</th>
<th>Zinc-blende</th>
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<tr>
<td>Ga in GaN</td>
<td>0.68</td>
<td>0.59</td>
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<tr>
<td>In in InN</td>
<td>0.66</td>
<td>0.58</td>
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