Analysis of x-ray absorption spectra of the K and $L_{2,3}$ edges of GaN within the FP-LAPW method

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Abstract

Gallium nitride, GaN, is a semiconductor material with several technological applications and therapeutic potential to inhibits the proliferation of tumor cells.

In this work we performed all electron self consistent calculations to obtain XANES spectra to be compared with experimental ones in order to study the electronic properties of these systems. The X-ray fine structure of hexagonal and cubic GaN were studied using the FP-LAPW method with the Tran and Blaha modified Becke-Johnson exchange potential within the DFT formalism.

The spectra obtained using the effect of the fractional core hole were compared with experimental cases obtaining very good agreement.

Keywords: core hole, K and $L_{2,3}$ edges, *ab-initio* calculations, XANES spectra

1. Introduction

Gallium nitride (GaN) is a large band gap semiconductor material that presents many interesting applications such as, emitters and detectors for visible and UV light

Besides, given the therapeutic potential of gallium, newer generations of gallium compounds are now in various phases of preclinical and clinical development. Gallium nitrate, inhibits the proliferation of tumor cells in vitro and in vivo and has shown activity against non-Hodgkin's lymphoma and bladder cancer in clinical trials

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GaN exhibits two polytypes, hexagonal (wurtzite structure) h-GaN and cubic (zincblende structure) c-GaN. The hexagonal polytype is stable and has been grown on various substrates. The cubic polytype is in fact metastable but it can be stabilized by a proper choice of the substrate, growth conditions and special preparation. However, because the local microstructure is almost the same in both polytypes, is possible to find in some areas of the layer a mixture of both phases.

Several experimental and theoretical studies

The XAS spectra, within the independent particle approximation (IPA), are proportional to the unoccupied part of the projected density of states (DOS) weighted by the transition probability from the core to the conduction states.

To our best knowledge the GaN X-ray absorption near edge structure (XANES) spectra are not yet calculated, for this reason we have calculated them to compare with measurements at the N K, Ga K and Ga $L_{2,3}$ edges. We use all electron calculations and fractional core hole within the Slater approximation.

2. Theoretical method

Wurtzite hexagonal structure (h-GaN) unit cell can be described by two lattice constants being a the length of the basal hexagon and c the height of the hexagonal prism. This structure consists of two hexagonal interpenetrating sub-lattices shifted by 5/8 of the cell height. The space group is $P6_3mc$.

The zincblende structure (c-GaN) has a cubic unit cell and contains four nitrogen atoms and four gallium atoms that form two interpenetrating lattices shifted 1/4 of the body diagonal.

We use all electron self-consistent calculations based on the scalar relativistic full-potential linearized augmented plane-wave basis set combined with local orbitals (FP-LAPW+lo), the calculations were carried out using the WIEN2k 14.2 package

The LDA and GGA functionals usually yield ground-state properties, which are in reasonable agreement with the experiments. However, this often is not the case for excited-state properties. For instance, it is well known that, very often, the band gap is strongly underestimated and sometimes even a metallic instead of an insulating state is obtained.

Methods that retain the computational efficiency of standard DFT but improve the spectroscopic properties are potentially of great interest. Further improvement has been achieved by a modified version (TB-mBJ)

We calculated near edge structure of X-ray absorption or emission spectra according to the formalism described by Neckel *et al.*

Slater‘s transition-state method enables to calculate excitation energies, this idea is adapted to insulators and semiconductors

In order to account for the core hole effect a supercell is needed to avoid the interaction between neighboring core holes

The XANES spectra were calculated for K and $L_{2,3}$ Ga and K N lines, and they were convoluted with a Lorentzian to account for lifetime broadening and resolution of the spectrometer.

2.1. The super cells

The artificial core hole - core hole interactions created by the periodic boundary conditions can be reduced by enlarging the distances between the core holes. Usually the Slater's method requires the use of supercells in order to do this.

First principles supercell and single cell calculations were used to analyze the hole-hole effect. We experimented with supercells of different sizes for the h-GaN structure, we used 2x2x1 and 2x2x2 and the final calculations were performed employing a 2x2x2 supercell of 32 atoms for the hexagonal polytype and 16 atoms for the cubic GaN polytype. We optimized both structures in order to obtain the lattice parameters.

The required precision in total energy was achieved by using a large plane-wave cutoff of $RK_{\max} = 8$, (where R is the muffin tin radii and $K_{\max}$ is the cutoff in the plane wave expansion of wave functional), resulting in a k-point sampling in the Brillouin zone (BZ) of about 500 points in h-GaN and 1000 points in the c-GaN supercells.

This corresponds to 200 k points in the irreducible wedge. The full analysis was carried out at the theoretical equilibrium volume based on the PBE calculations. The atomic sphere radii (in a.u.) used were 1.95 for Ga and 1.65 for N.

3. Results and discussion

In this work we performed the self consistent *ab-initio* calculations to optimize both structures. In h-GaN the total energy is slightly lower than in c-GaN as we expected, being h-GaN the equilibrium structure.

The XANES spectra were calculated using the non local TB-mBJ potential, in h-GaN and c-GaN with fractional core holes and compared with the experimental data

First we analyze the h-GaN spectra. In Figure 1 the calculated Ga K edge is plotted and in this case we find the full core hole is the best fit to the experimental XANES spectrum measured by Schuber *et al.*

In Figure 2 the calculated Ga p DOS and, broadened and unbroadened Ga K spectra, are shown compared to the experimental spectrum produced by Schuber *et al.*

The p DOS in the hexagonal structure has been divided into its px+py and pz components.

In Figures 3 and 4 we show the projected px+py and pz DOS as a function of the core hole for the same Ga K edge. It is done to analyze the influence of the increasing core hole in the partial DOS contributions.

We consider the peaks A, B, C, D in the first group of the p DOS. The A and C peaks show a similar contribution of both pz and px+py, and they grow when the core hole increases. While the B peak shows a bigger contribution of pz only and grows as the core hole increases. For the D structure to the right of the C peak, we observe that the px+py contribution decreases with the increasing core hole. The rest of the DOS is not changing with the core hole increment. A similar analysis can be done in all other cases.

In Figure 5 a comparison of the Ga s and d DOS and, broadened and unbroadened Ga $L_{2,3}$ spectra, are shown. The $L_{2,3}$ represent a combination of transitions to s states near threshold and d states at higher energies. In the calculated $L_{2,3}$ edge the best fit to the experiment made by Chiou *et al.*

In Figure 6 a comparison of the N p DOS, for the N K edge and the spectra are shown.

In the calculated N K edge the best fit to the experiments made by Takeuchi

The same edges, Ga K, Ga $L_{2,3}$ and N K, were calculated for c-GaN.

In the Ga K edge case we do not have experimental data to compare with, so according to Slater we chose 0.5 core hole. In Figure 7 the Ga p DOS and Ga K spectra are shown for the 0.5 core hole.

For the calculated Ga $L_{2,3}$ the full core hole is the best fit with the experimental data measured by Lowniczak *et al.*

The calculated N K edge is compared with the experiment made by Katsikini *et al.*

The lattice parameters of the h-GaN structure obtained self-consistently are: a = 3.219 Å and c = 5.264 Å and the lattice parameter of the c-GaN structure obtained is a = 4.556 Å. The theoretical equilibrium volumes obtained by our calculations using PBE are slightly larger than the experimental ones. Our result for the cubic structure compares well with the one

obtained by Haas *et al.*

Using the TB-mBJ method a band gap of 3.0 eV is obtained in agreement with Koller *et al.* which is much closer to the experimental 3.2 eV band gap, compared to the 1.8 eV band gap we produced with the PBE calculations. Using TB-mBJ method for c-GaN a band gap of 2.7 eV is obtained compared to the 1.4 eV band gap we produced with the PBE calculations.

4. Conclusions

The DFT is formally a theory for the ground state but gives at least a good estimate in properties that involve excited energy states like absorption or emission spectra

The XANES spectra were calculated for both structures of GaN with different core holes and compared with the experimental results

XANES provides information about the electronic structure and orbital character of the conduction band of materials, together with the DOS calculations, these techniques indicate a material overall electronic structure as well as the energy scale in the electronic structure.

In h-GaN polytype for the Ga K edge and Ga $L_{2,3}$ edge the best fit is obtained for the full core hole and for the N K edge the 0.7 core hole is better compared to the experimental XANES spectra.

In c-GaN structure for Ga $L_{2,3}$ and N K edges the full core hole is the best fit to the experimental spectra. For c-GaN Ga K we were not able to find an experiment to compare.

Our results for the fractional core holes from XANES spectra are similar to the ones shown by Lazar *et al.*

The TB-mBJ method improves the value of the calculated band gap produced by the PBE calculations obtaining results very close to the experiments.

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Figure 2: Broadened and unbroadened XANES Ga K edge in h-GaN compared to Ga p-projected DOS calculated using TB-mBJ potential. The XANES beyond the edge onset is plotted, while the DOS is plotted above the Fermi level.

Figure 3: Ga px+py projected DOS calculated for the different core holes.

Figure 4: Ga pz projected DOS calculated for the different core holes.

Figure 5: Broadened and unbroadened XANES Ga $L_{2,3}$ edge in h-GaN compared to Ga s and d-projected DOS. The XANES beyond the edge onset is plotted, while the DOS is plotted above the Fermi level.

Figure 6: Broadened and unbroadened XANES N K edge in h-GaN compared to N p-projected DOS. The XANES beyond the edge onset is plotted, while the DOS is plotted above the Fermi level.

Figure 7: Broadened and unbroadened XANES Ga K edge in c-GaN compared to Ga p-projected DOS. The XANES beyond the edge onset is plotted, while the DOS is plotted above the Fermi level.

Figure 8: Broadened and unbroadened XANES Ga $L_{2,3}$ edge in c-GaN compared to Ga s and d-projected DOS. The XANES beyond the edge onset is plotted, while the DOS is plotted above the Fermi level.

Figure 9: Broadened and unbroadened XANES N K edge in c-GaN compared to N p-projected DOS. The XANES beyond the edge onset is plotted, while the DOS is plotted above the Fermi level.