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Anisotropic spectroscopy of nitrogen K-edge in group-III nitrides

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Ab initio calculation of nitrogen K-edges for use in the core-level spectroscopy of industrially important group-III nitrides (AlN, GaN, InN) has been carried out systematically including the core-hole effect. The theoretical spectra for transition into final states with $p_{x,y}$ and p_z symmetries are in good agreement with the available anisotropic electron energy-loss measurements. Our spectra can be used as "fingerprints" to characterize the group-III nitrides, for example, not only to distinguish between different polymorphs of group-III nitrides, but also to identify the presence of surface oxidation. We have also presented our simulated results in terms of an orientation-average spectrum and a sample orientation-dependent dichroic spectrum for future reference. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1691498]

Group-III nitrides (AlN, GaN, and InN) are important semiconducting materials for optoelectronic as well as high-temperature and high-power microelectronic device applications.[1] These nitrides can exist in a number of polymorphic forms with the anisotropic wurtzite (w) structure being the thermodynamically stable structure of bulk materials under ambient conditions, hence most widely used.[1] The intimate connection between the unoccupied local densities of states (LDOS) and the core-level excitation spectrum allows electron energy-loss spectroscopy (EELS) or x-ray absorption spectroscopy (XAS) to be used to study the electronic structure, hence crystal structure of the materials.[2–12] For example, the electron energy-loss near-edge structure or the x-ray absorption near-edge structure of nitrogen K-edges has been used as a "fingerprint" to identify the chemical environment of the nitrogen atom,[5–10] the phase composition,[11,12] as well as phase orientations.[11,12]

In anisotropic wurtzite structures, because of the dipole selection rule, the experimental K-edge spectra are normally composed a mixture of p_{xy} and p_z components with a varying ratio determined by the experimental condition.[13,14] This complication means that great care should be exercised in the direct use of fine structure of core-level spectroscopy as the fingerprint method for characterizing the different nitrides. On the other hand, the availability of the symmetry-resolved nitrogen K-edges not only can help with the application of the fingerprint method as reference standards, but they can also be used directly to study the orientation as well as phase abundance of the wurtzite nitride crystals.

Experimental determination of symmetry-resolved N K-edge spectra has been carried out using XAS[4,5,15,16] and EELS[9,17] methods, but with conflicting results. For example, a significant discrepancy can be found from the reported XAS[15] and EELS[17] result of the p_z symmetry projected unoccupied LDOS in AlN. Theoretical investigations have also created some confusion: using the full potential linearized augmented plane wave (FPLAPW) method, a clear discrepancy is reported between experimental EELS results and the calculated p_z symmetry final states, even with the inclusion of core-hole effects for GaN[9] in contrast to the good agreement achieved in AlN.[17] In view of the experimental difficulties involved, we have carried out a systematic theoretical simulation of symmetry-resolved K-edge spectra for anisotropic wurtzite structure, using an *ab initio* pseudopotential plane wave method with a proper treatment of the core-hole effect. These spectra compare well with available EELS measurements. Using these simulated spectra, we can explain the discrepancy of the EELS[17] data with polarized XAS[4,15] data for AlN as due to a surface oxidation effect.

The calculation is performed using an *ab initio* pseudopotential plane wave method. Ultrasoft Vanderbilt pseudopotentials were employed, using the gradient-corrected functional exchange-correlation approximation. To include the core-hole effect[18–21] in our calculation, a pseudopotential with an atomic configuration $1s^1 2s^2 2p^4$ was specially constructed to represent the nitrogen atom at which the deep core hole is localized. To minimize the interaction between the nearest excited centers in the periodic crystal structure, we have experimented with supercells of different sizes, with the final results employing a $2\times2\times2$ supercell (32 atoms) in the calculation. The wave functions were expanded in plane waves with an energy cutoff of 380 eV and a $4\times4\times4$ equivalent Monkhorst–Pack k-point mesh was used. Nitrogen K-edge spectra corresponding to $1s$ to p_{xy} or p_z transitions were simulated by the LDOS with p_{xy} or p_z symmetry projected on the excited nitrogen atom, with the choice of projection-sphere radius[19] similar to the radial extension of N $1s$ wave function. Tests indicate that the choice of the cutoff radius is not a sensitive factor in the calculation when it is small.

From our results with and without the core-hole correction, it is found that the core-hole influence on the nitrogen K-edge spectra is not significant, especially for the energy region 15 eV above the threshold. This means that a standard ground-state calculation may be used to obtain an approximate nitrogen K-edge spectra,[2,4] particularly with regard to the number of peaks in the spectra. However, the inclusion of the core-hole effect is essential in all three compounds to predict the precise energy and relative intensities of the experimental spectra precisely. The theoretical spectra including core-hole effects are shown in Fig. 1. The energy scale is

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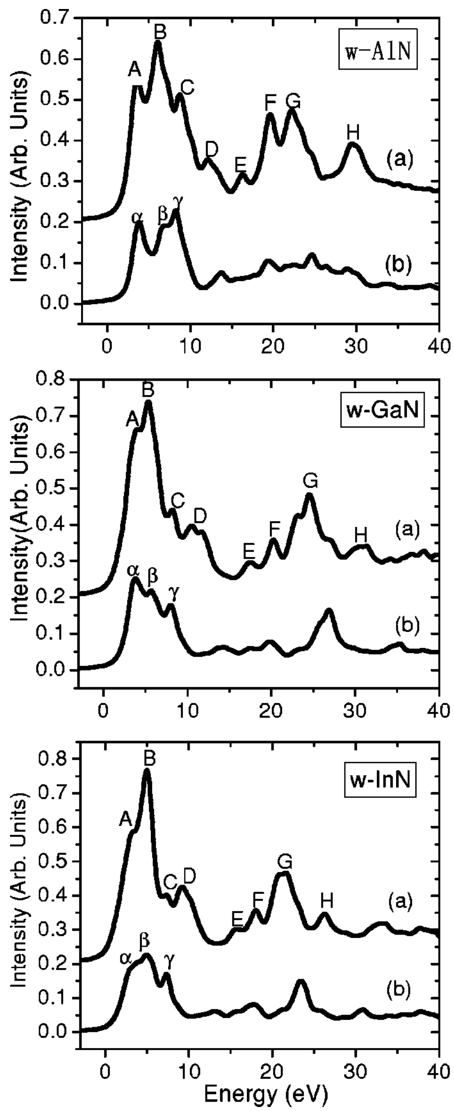

FIG. 1. The theoretical nitrogen K-edges of wurtzite crystals of AlN, GaN, and InN; the spectra with p_{xy} (a) and p_z (b) final states are plotted separately.

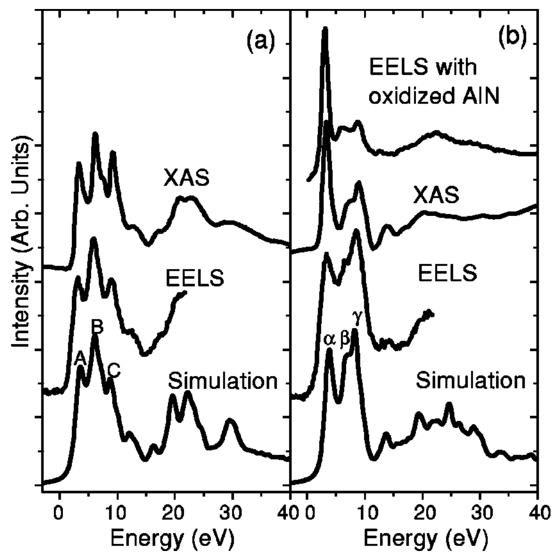

FIG. 2. The comparison of our simulated spectra for nitrogen K-edge in AlN with spectra measured using XAS from Ref. 15 and EELS from Ref. 17. The panel (a) shows the spectra corresponding to p_{xy} final states and panel (b) for the p_z final states. EELS data of a partial oxidized AlN foil from Ref. 10 has also been included in the panel (b) for comparison.

relative to the Fermi level. The calculated spectra have been convolved with a Lorentz function for lifetime broadening and the experimental energy resolution with a fixed width of 1.0 eV, an easily achievable energy resolution for modern EELS attachment in a (scanning) transmission electron microscope. This means that our calculated spectra may have overstated the fine structure at the energy region far above the absorption threshold, an effect that can be easily accounted for by additional spectral broadening there. In Fig. 1, all the spectra corresponding to the p_{xy} final states have been shifted upward by a constant value for easy visualization. The main features were labeled as **A**, **B**, **C**, etc. for the p_{xy}-symmetry projected spectra, and α, β, γ, for the p_z-symmetry projected spectra.

The three nitrogen K-edges have similar general envelopes, as expected for the similar bonding environments of the excited nitrogen atom, (i.e., bonding to group-III cations in the wurtzite structures), but they can still be used as fingerprints because significant differences still exist in the fine structure symmetry-resolved spectra, particularly among the p_z-projected spectra. For example, the first three intense features (α, β, and γ) form fine structures that change from being "hollow-like" in AlN and "down-hillside-like" in GaN, to being "mountain-like" in InN. In comparison, systematic changes in the fine structure composed of **A**, **B**, and **C** in the p_{xy}-projected spectra is also visible, but at high energy resolution. For example, compared with the most prominent peak **B**, the relative intensities of the peak **C** decrease systematically from AlN and GaN to InN. At high energy, a common feature of the spectra of the three compounds is the significant difference in the peak energy between the p_{xy}- and p_z-projected spectra, reflecting the anisotropic atomic structure.

Experimentally, anisotropic spectra can be probed by either x-ray- or electron-induced core-level excitation. When the electric field (**E**) of the absorbed light in XAS or the momentum transfer vector (**q**) in EELS is perpendicular to the **c** axis of the crystals ($\mathbf{E}\perp\mathbf{c}$ or $\mathbf{q}\perp\mathbf{c}$), the transition from N $1s$ level to the p_{xy}-symmetry projected states is probed. If the electric field of the absorbed light or the momentum transfer is parallel to the **c** axis ($\mathbf{E}\|\mathbf{c}$ or $\mathbf{q}\|\mathbf{c}$), spectra corresponding to p_z-symmetry-projected final states can be acquired. In transmission EELS, all atoms along the electron-beam path contribute equally to the resulting spectra, making the surface effect almost negligible. The crystal structure of the thin foil used for EELS study can also be confirmed by independent electron diffraction analysis, so that the EELS data should be more representative of the bulk materials. The anisotropy in EELS arises because the direction of the momentum transfer vector is controlled by scattering angle as well as the direction of the incident electron beam.[13,14,22] Pure symmetry projected spectra are obtained by either adopting special scattering and collection condition[23] or by data processing.[13,14] Our theoretical spectra agree well with both the reconstructed $\mathbf{q}\perp\mathbf{c}$ and $\mathbf{q}\|\mathbf{c}$ EELS spectra of AlN[17] and GaN.[9] An example of such comparison for AlN can be found in Fig. 2. It is interesting to note that a sufficiently large supercell is essential to obtain this agreement. When we use the smaller $2\times2\times1$ supercell size for GaN as Ref. 9, the result is different, indicating that mutual interaction between nearest excited centers is still not sufficiently suppressed.

With x-ray excitation, the direction of the electric field is transverse to the beam direction, so that anisotropic measurements can be performed if x-ray absorption or reflectivity experiments can be carried out for both normal- and glancing-angle incidence. Lawniczak-Jablonska *et al.* have carried out such a systematic measurement of nitrogen K-edge spectra for AlN, GaN, and InN.[4,15] Figure 2 shows the comparison of our theoretical spectra in AlN with the XAS data. While the agreement in the $\mathbf{E}\perp\mathbf{c}$ spectra is good, a glaring difference is observed in the $\mathbf{E}\parallel\mathbf{c}$ spectra. Since our data are in good agreement with the EELS spectra and a comparable calculation using a FPLAPW method,[17] we believed that the XAS data in glancing angle ($\mathbf{E}\parallel\mathbf{c}$), being more surface sensitive, may be sampling a microstructure different from that probed by XAS done at normal incidence ($\mathbf{E}\perp\mathbf{c}$) where the x ray can penetrate deep into the material. As shown also in Fig. 2, a sharp feature at the onset of the nitrogen K-edge can also be detected in partially oxidized AlN using EELS.[10] A reasonable explanation for the discrepancy between the $\mathbf{E}\parallel\mathbf{c}$ XAS spectrum and our calculated spectra is the surface oxidation of the AlN crystal used.

Angular resolved x-ray absorption measurement has been used to find the abundance of the wurtzite structure over cubic structure of GaN, as well as finding the relative orientation of w-GaN thin film on the surface.[11,12] The example just presented illustrates the importance of characterizing the surface quality of thin films and the importance of having reliable reference spectra in this regard. This also applies to EELS measurement near defects in the crystals.

One advantage of the nitride semiconductors is the ability for them to form alloy compound semiconductors so that the physical properties can be turned continuously. Our systematic calculation of anisotropic spectra for the three important nitrides provides the theoretical basis for extending the anisotropic measurement to alloy materials. In such materials, one wishes to separate the chemical alloying effect from the anisotropic effect. This can be achieved easily by working in terms of the rotationally averaged and the corresponding dichroic spectra,[24] respectively (see Fig. 3). The rotationally averaged spectra can be acquired at the magic-angle condition[13] for both XAS and EELS. The average spectra can also be easily compared with other polymorphs of nitride without considering the effect of specimen orientation, and for studying doping induced effect, for example. On the other hand, the fine structure in the dichroic spectra may be more sensitive to the strain effect in the materials.

In summary, we have provided reliable spectra of the nitrogen K-edges in wurtzite AlN, GaN, and InN, including the core-hole effects. Our calculation is in good agreement with the reported anisotropic EELS measurement of AlN and GaN. Using our calculation as a fingerprint, the possible oxidation influence to the reported $\mathbf{E}\parallel\mathbf{c}$ XAS spectra in AlN is identified.

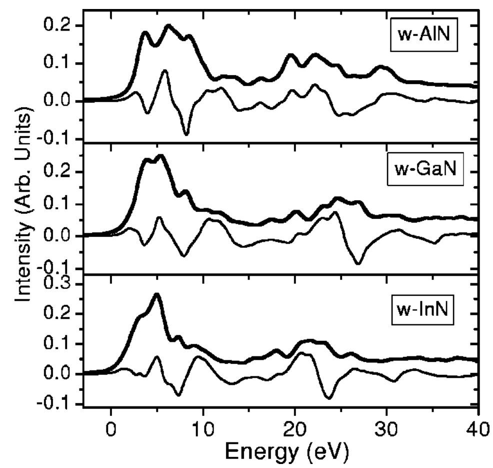

FIG. 3. Averaged spectra (thick line) and dichroic spectra (thin line) for wurtzite AlN (a), GaN (b), and InN (c).

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[1] H. Morkoç, *Nitride Semiconductors and Devices* (Springer, Berlin, 1999).
[2] K. A. Mkhoyan, J. Silcox, E. S. Alldredge, N. W. Ashcroft, H. Lu, W. J. Schaff, and L. F. Eastman, Appl. Phys. Lett. **82**, 1407 (2003).
[3] S. Y. Li and J. Zhu, J. Cryst. Growth **203**, 473 (1999).
[4] K. Lawniczak-Jablonska, T. Suski, I. Gorczyca, N. E. Christensen, K. E. Attenkofer, R. C. C. Perera, E. M. Gullikson, J. H. Underwood, D. L. Ederer, and Z. Liliental Weber, Phys. Rev. B **61**, 16623 (2002).
[5] L.-C. Duda, C. B. Stagarescu, J. Downes, K. E. Smith, D. Korakakis, T. D. Moustakas, J. Guo, and J. Nordgren, Phys. Rev. B **58**, 1928 (1998).
[6] Y. Xin, E. James, I. Arsian, S. Sivananthan, N. D. Brownig, S. J. Penneycook, F. Omnès, B. Beaumont, J-P. Faurie, and P. Gibart, Appl. Phys. Lett. **76**, 466 (2000).
[7] M. Benaissa, P. Vennéguès, B. Beaumont, P. Gibart, W. Saikaly, and A. Charai, Appl. Phys. Lett. **77**, 2115 (2000).
[8] V. Lordi, V. Gambin, S. Friedrich, T. Funk, T. Takizawa, K. Uno, and J. S. Harris, Phys. Rev. Lett. **90**, 145505 (2003).
[9] V. J. Keast, A. J. Scott, M. J. Kappers, C. T. Foxon, and C. J. Humphreys, Phys. Rev. B **66**, 125319 (2002).
[10] M. MacKenzie and A. J. Craven, J. Phys. D **33**, 1647 (2000).
[11] M. Lübbe, P. R. Bressler, W. Braun, T. U. Kampen, and D. R. T. Zahn, J. Appl. Phys. **86**, 209 (1999).
[12] M. Katsikini, E. C. Paloura, and T. D. Moustakas, J. Appl. Phys. **83**, 1437 (1998).
[13] N. K. Menon and J. Yuan, Ultramicroscopy **74**, 83 (1998).
[14] N. D. Browning, J. Yuan, and L. M. Brown, Ultramicroscopy **38**, 291 (1991).
[15] K. Lawniczak-Jablonska, T. Suski, Z. Liliental-Weber, E. M. Gullikson, J. H. Underwood, R. C. C. Perera, and T. J. Drummond, Appl. Phys. Lett. **70**, 2711 (1997).
[16] W. R. L. Lambrecht, S. N. Rashkeev, B. Segall, K. Lawniczak-Jablonska, T. Suski, E. M. Gullikson, J. H. Underwood, R. C. C. Perera, J. C. Rife, I. Grzegory, S. Porowski, and D. K. Wickenden, Phys. Rev. B **55**, 2612 (1997).
[17] G. Radtke, T. Epicier, P. Bayle-Guillemaud, and J. C. Le Bosse, J. Microsc. **210**, 60 (2003).
[18] D. N. Jayawardane, C. J. Pickard, L. M. Brown, and M. C. Payne, Phys. Rev. B **64**, 115107 (2001).
[19] S. Köstlmeier and C. Elsässer, Phys. Rev. B **60**, 14025 (1999).
[20] S.-D. Mo and W. Y. Ching, Appl. Phys. Lett. **78**, 3809 (2001).
[21] I. Tanaka, T. Mizoguchi, T. Sekine, H. He, K. Kimoto, T. Kobayashi, S.-D. Mo, and W. Y. Ching, Appl. Phys. Lett. **78**, 2134 (2001).
[22] J. Taftø and J. Zhu, Ultramicroscopy **9**, 349 (1982).
[23] R. D. Leapman and J. Silcox, Phys. Rev. Lett. **42**, 1361 (1979).
[24] J. Yuan and N. K. Menon, J. Appl. Phys. **81**, 5087 (1997).