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Nitrogen and aluminum near K-edge absorption measurements of wurtzite AlN, GaN and InN, and their ternary compounds (AlGaN, InGaN and InAlN) at various molar fractions have been performed using synchrotron radiation. Using the linear polarization of synchrotron radiation, absorption measurements with different incident light angles were also performed. The spectral distribution of the nitrogen K absorption spectra clearly depends on both the incident light angles and the molar fractions of the samples. That of the aluminum K absorption spectra also shows the clear angle dependence, but it does not show the drastic molar dependence. Spectral shape comparisons among the various molar fractions, different incident angles and between the two ion sites are discussed. The numerical component analysis of the K absorption spectra is also presented.

Introduction Since the core levels are strictly localized in space, inner core excitation can select the specific ion site in the materials and give us site-specific information. This means that it is a useful method to investigate binary or ternary compounds. The spectrum near the K-core absorption edge, which excites the 1s electrons to the conduction band, represents the unoccupied p partial density of states (p-PDOS) according to the selection rule. Such kind of works for III–V nitride semiconductors has been reported by several studies in Refs. [1, 2] and references therein. They indicate the good overall agreement between the experimental and calculated results. Furthermore, since the synchrotron light source has linear polarization, the unoccupied p-PDOS is resolved into the in-plane and the out-of-plane states.

In our previous work [1], we reported the soft X-ray absorption spectra around nitrogen K (N-K) and aluminum K edge (Al-K) of the wurtzite AlN, GaN and their ternary compounds $Al_xGa_{1-x}N$. All samples clearly showed the incident light angle dependence of the absorption spectra, which directly reflected the anisotropy of the unoccupied p-PDOS. Then we presented a numerical component analysis to separate the experimental K-absorption spectrum (KAS) into three partial spectra which correspond to in-plane, out-of-plane and angular independent components. The comparison of the spectral feature among the different molar fraction (x) samples is one of the standards to investigate the peak identifications in the spectra. Therefore, the combination of those two techniques with the ion-site specific nature of the core absorption measurement becomes effective to investigate the structures of the unoccupied DOS. In this paper, to investigate the structures of the unoccupied p-PDOS of the III–V nitrides, both the N-KAS and Al-KAS of the whole III–V nitrides (AlN, GaN and InN) and their compounds ($Al_xGa_{1-x}N$, $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$) were carried out.

Experimental Procedure All samples are wurtzite thin films that have their *c*-axis perpendicular to the film surface. They were grown by the MOCVD method. All the $Al_xGa_{1-x}N$ ($0.05 \leq x \leq 1.0$) and $In_xGa_{1-x}N$ ($x \leq 0.15$) samples were fabricated on SiC substrates at RIKEN, and GaN, $In_xAl_{1-x}N$ and $In_xGa_{1-x}N$ ($0.02 \leq x \leq 1.0$) were grown on α-Al_2O_3 substrates at Nichia Chemical Industries Ltd., Meijo University and Fukui University, respectively. The sample thickness is between 0.1 and 4 μm. The molar fraction x was determined by the lattice constant or luminescence peak of each sample.

The N-K and Al-K absorption measurements were performed at the beamlines BL4B and BL8B1, BL1A and BL7A of UVSOR (synchrotron radiation light source), Institute for Molecular Science. All the experiments were performed at room temperature using the total photoelectron yield method that was measuring the sample drain current in the vacuum chamber. The incidence angle θ is defined as the angle between the incident light and the normal axis of the sample surface. The configuration between the electric field of the incidence light **E** and the rotation axis is p-polarization. To avoid a charge-up of the sample surface for the threshold energy determination experiment at $\theta = 0$, an Au mesh and a Cu box were used to cover the sample surface.

Results and Discussion Figure 1a shows the N-KAS of the $Al_xGa_{1-x}N$, $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ and Fig. 1b shows the Al-KAS of $Al_xGa_{1-x}N$ and $In_xAl_{1-x}N$. The param-

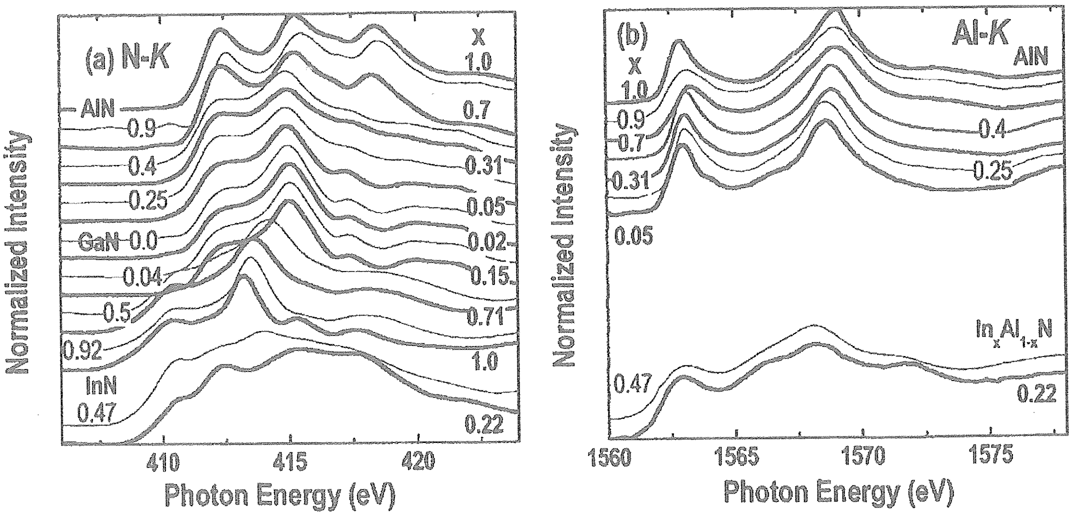

Fig. 1. Normal incidence a) nitrogen K absorption spectra of $Al_xGa_{1-x}N$, $In_xGa_{1-x}N$ and $In_xAl_{1-x}N$ (from top to bottom) and b) aluminum K absorption spectra of $Al_xGa_{1-x}N$ and $In_xAl_{1-x}N$

eter x of each spectrum corresponds to the molar fraction of Al or In of the respective ternary compound sample. The intensity is normalized at the maximum peak. The spectrum distribution of both Figs. 1a and b are in agreement with the other works [1, 2]. Many peaks and shoulders are obviously seen in each spectrum of Figs. 1a and b except the case of $In_xAl_{1-x}N$ samples that show a relatively structure-less feature. This may correspond to the X-ray diffraction results which suggest that c-axis fluctuations of $x = 0.22$ and 0.47 samples are about three and ten times larger than those of the typical $Al_xGa_{1-x}N$ samples, respectively. The N-KAS, drastically but continuously, changes its feature with x, however Al-KAS basically does not change its feature with x. As pointed out in our previous work for AlGaN [1], this difference is mainly due to the environmental difference between cation and anion. Since the substituted ions are always cation, the nearest neighbour ions of the N ion have probability of substitution. On the other hand, those of the Al ion are always N ions. The continuous change of the spectral distribution with x in the N-KAS suggests that the unoccupied p-PDOS feels the long-range cation substitution. The insensitiveness to x of the Al-KAS suggests that the Al 1s electron transition is almost intra-atomic. These results represent that the unoccupied p-PDOS mainly consists of cation p states. The similar explanation can be applied to the threshold energy shift. The threshold energy of the N-K absorption systematically shifts to the lower energy side from AlN to InN. An obvious shift can be seen in the InGaN region. However, the threshold energy of the Al-K absorption has no shift beside the spectral broadening in the InAlN region.

Both the N-KAS and Al-KAS of all samples except $In_{0.47}Al_{0.53}N$ change their spectral distributions with θ. The intensities of the peaks in the $In_{0.22}Al_{0.78}N$ KAS indicate a weak θ dependence relative to those in other samples. However, it is noted that this dependence of the intensity of each peak on θ in Figs. 1a and b is completely inversion related between $In_{0.22}Al_{0.78}N$ and the other AlGaN (and InGaN) samples. For example, the intensity of the peak around 1569 eV of AlN (maximum peak) increases its intensity with decreasing θ, however that of $In_{0.22}Al_{0.78}N$ increases with increasing θ. The similar inverse relation is observed in the N-KAS. There are not enough results to recognize this phenomenon, but this result suggests that the p-PDOS in the conduction band switches its anisotropy twice between AlN and InN. It may also suggest that the weak or no anisotropy of the KAS of InAlN is due to not only the crystallinity but also this complicated band configuration.

The partial spectra decomposed numerically from N-KAS and Al-KAS of AlN are seen in Figs. 2a and b, respectively. Details of the numerical decomposition for $Al_{0.4}Ga_{0.6}N$ are described in the previous work [1]. The spectra labelled XY, Z, NA and T correspond to in-plane, out-of-plane, angular independent components of the unoccupied p-PDOS at N- or Al-sites and the calculated KAS at $\theta = 35.26°$ using XY, Z and NA spectra. Similar spectral distributions of those partial spectra are seen in both the N-KAS and Al-KAS of all samples except InAlN. In case of $In_{0.22}Al_{0.78}N$, XY and Z partial spectra are weak and exchange their spectral distributions with each other. There are two in-plane subbands and two out-of-plane subbands at N-site and they correspond to the peaks in Fig. 1a. Then, the maximum peak in each N-KAS has the similar origin and consists of in-plane p bonding. Both the lower and higher side peaks relative to the maximum peak consist of out-of-plane p bonding. In the $Al_xGa_{1-x}N$ region, the maximum peak becomes the dominant peak with decreasing x. However,

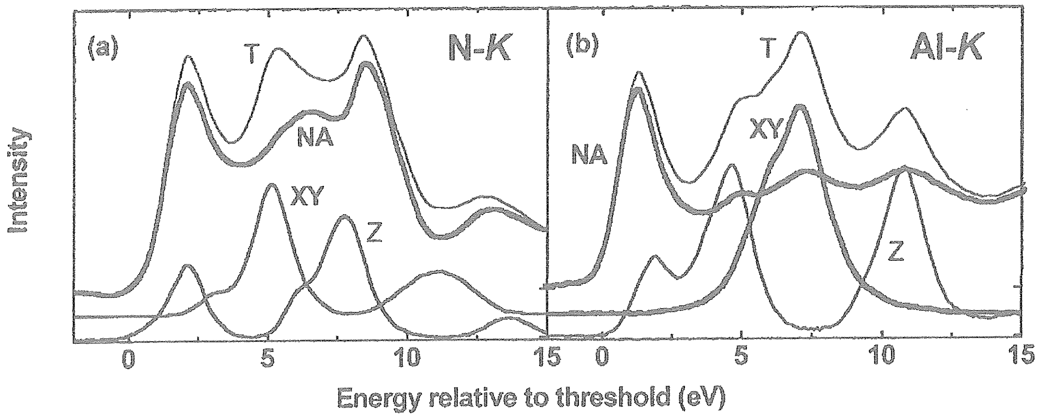

Fig. 2. Partial spectra decomposed numerically from a) nitrogen K and b) aluminum K absorption spectra of AlN

decomposition reveals that the maximum peak increase is mainly due to the increasing NA component with decreasing x. In the lower x $In_xGa_{1-x}N$ region ($x < 0.71$), these partial spectra resemble those of GaN. In the higher x $In_xGa_{1-x}N$ region, the lowest peak disappears in the Z partial spectrum. The threshold energy shift between normal and parallel incidence N-KAS is reported [2], but we cannot observe it within the limitation of $\theta \leq 60°$. If one defines the intensity ratio XY (or Z) to NA spectra as an index of the p bonding anisotropy, the anisotropy becomes weak with decreasing x in $Al_xGa_{1-x}N$ region and almost constant in lower x $In_xGa_{1-x}N$ region. There are three out-of-plane subbands and one in-plane subband at Al-site and they correspond to the peaks and shoulder in Fig. 1b. The maximum peak also consists of out-of-plane bonding. As pointed out in the previous work [1], except for the lowest peak in Z spectrum, a peak in the XY spectrum at N-site correspond to a Z peak at Al-site and *vice versa.* This is because the different bonds are formed in-plane and out-of-plane [2].

Conclusions The N-K and Al-K absorption measurements of wurtzite AlN, GaN and InN, and their ternary compounds at various molar fractions have been performed using synchrotron radiation. The KAS is almost directly compared with the unoccupied p-PDOS. The spectral distribution of N-KAS, drastically but continuously, changes with x among AlN, GaN, and InN. On the other hand, that of Al-KAS has no drastic x dependence. The threshold energies of N-KAS and Al-KAS show x dependence and x independence, respectively. They are explained as the enviroment difference between cation and anion sites.

Since all samples except $In_{0.47}Al_{0.53}N$ show anisotropy of the unoccupied p-PDOS, the spectral distributions of different θ are different with each other. The intensity dependence of a peak in the N-KAS and Al-KAS on θ is essentially similar for any x of all the samples except InAlN, but the inverse dependence is observed in $In_{0.22}Al_{0.78}N$. According to the numerical decomposition of the KAS, the maximum peak in each N-KAS and Al-KAS has similar origin, respectively. These peaks consist of in-plane p bonding.

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