The Absolute Indium Composition in InGaN/GaN Quantum Wells

III-nitride semiconductors have been realized for many commercial light emitters and detectors in short wavelength regime over last decade. The commercialization becomes successful due to the high bright blue-green light emission and ultra rut lasing from III-nitride materials. In most III-nitride based light emitting devices, InGaN thin films and multiple quantum wells (MQWs) are widely used as active layers since they have a direct optical band gap that can be tuned from visible to ultraviolet spectral range. Since the band gap is determined by the indium concentration and lattice strain of the crystalline lattice, the direct determination of these two structural parameters is very important. Despite a great deal of research on InGaN alloy systems, however, it is surprising that there are few experimental reports on such studies.

Regular X-ray diffraction (XRD) using X-rays of fixed energy can be employed to obtain crystalline lattice parameters with sub-angstrom sensitivity but is insensitive to composition. Often, the chemical composition of an alloy system is indirectly estimated from X-ray scattering profile by applying Vegard's law that relates the lattice parameters to the chemical composition. Applying Vegard's law to thin films or MQWs can be difficult or even misleading due to the lattice strain that alters the lattice parameters. Other methods of chemical analysis such as XPS and RBS measure average composition rather than the chemical composition incorporated in the crystalline lattice that is relevant to the band gap.

Anomalous X-ray scattering (AXS) is a synchrotron-based technique that can provide both chemical and structural information simultaneously. Atomic scattering factor f is composed of non-resonant Thomson scattering factor f_0 and anomalous scattering factor $\triangle f$, and generally expressed as $f(\vec{Q},E) \approx f_0(\vec{Q})+\triangle f(E)$ due to the weak wavevector dependency of $\triangle f$. $\triangle f$ varies anomalously both in magnitude and phase as the probing X-ray energy approaches binding energies of core electrons of a specific element. Consequently, the X-ray scattering profile changes as the X-ray energy is tuned across an absorption edge of the element. The change of the scattering intensity of a Bragg reflection is directly related to the chemical content of the element incorporated in the crystalline lattice. Measuring the anomalous change of the X-ray scattering intensity across an absorption edge is called AXS. In this report, we present an AXS experiment at the indium K absorption edge to determine the indium composition incorporated in the crystalline lattice of InGaN films and InGaN/GaN multiple quantum wells.

InGaN and InGaN/GaN MQWs samples were grown on n-type GaN (1.2 μm) deposited on sapphire (0001) substrates in a vertical flow type MOCVD chamber using trimethylgallium (TMGa), TMIn, and ammonia. Two different growth temperatures, 780 ℃ (InGaN #A and MQW #A) and 740 ℃ (InGaN #B and MQW #B) were employed to control the In composition. It is known that more In atoms are incorporated at lower growth temperatures. Both the InGaN films and the MQWs were undoped. The InGaN thin films are about 1000 Å thick, and the MQWs consist of the well-barrier stacks with about 150 Å stack period. The AXS measurements were carried out at Taiwan contract beamline 12B2 at SPring-8, Japan. The energy of the probing X-rays was controlled by a double bounce Si (311) monochromator.

We first carried out the AXS measurements on the InGaN films (single layer) across the indium K absorption edge, 27.94 keV (0.444 Å). Near the indium K-edge, only indium atoms show anomalous behavior because the X-ray energy is far from other absorption edges. We selected the InGaN (0006) peak since it is well resolved from the diffraction signal of the substrate GaN. It also

produces more accurate results since the resonant to non-resonant ratio is larger due to the decrease of the Thomson scattering factor at high-Q. Fig. 1 shows the InGaN (0006) profile, and the AXS spectra, the intensity variation as a function of the X-ray energy measured at the peak of the InGaN (0006) marked in Fig. 1(a, b). The AXS shown in Fig. 1(c, d) exhibits an intensity cusp at the indium K-edge whose magnitude is directly related to the indium composition. InGaN #B with more indium shows a larger intensity cusp than InGaN #A.

Based on the kinematical approximation assuming that the InGaN films are random alloys, the scattering intensity is described by

$$I(\vec{Q},E) = A(\vec{Q},E)S(\vec{Q}) \cdot |(1-x)f^{Ga}(\vec{Q})+xf^{In}(\vec{Q},E) + e^{i\varphi_N}f^{N}(\vec{Q})|^2, \quad (1)$$

where A includes overall proportional constant including Lorentz-polarization, absorption, and illuminated area corrections, S is the structure factor, fs are atomic form factors, and φ_N is the relative phase of nitrogen atoms. Across the relatively narrow energy range, all other factors than f In are nearly constant at a fixed momentum transfer Q. The indium composition, x is simply determined by fitting the AXS spectra to Eq. (1).

The absolute indium composition of InGaN #A(#B), thus obtained, is 11.2±1.1% (17.8±1.2%). The solid lines show the results of the fits. The error bars, the resolution of the composition determination, are decided by finding the root of $\triangle\chi^2 = 1$ (increase in the goodness of the fit) numerically. The absolute indium composition obtained by the AXS measurement is compared to the results of the regular XRD where the value of the Poisson's ratio is required. The XRD analysis yields a value close to the absolute composition determined by the AXS using Poisson's ratio, $\nu \approx 0.23$ for both the samples.

To apply the AXS technique to the InGaN/GaN MQW samples requires additional care. The AXS spectra of the MQW samples measured at the (0006) reflection are shown in Fig. 2. For a multi-layer the scattering intensity is described by,

$$I = MLF \cdot |S_{InGaN}+S_{GaN} \cdot e^{iQ_Z \cdot \Lambda/2}|^2 = \frac{\sin^2(Q_Z N\Lambda/2)}{\sin^2(Q_Z\Lambda/2)} \cdot |S_{InGaN}+S_{GaN} \cdot e^{iQ_Z \cdot \Lambda/2}|^2, \quad (2)$$

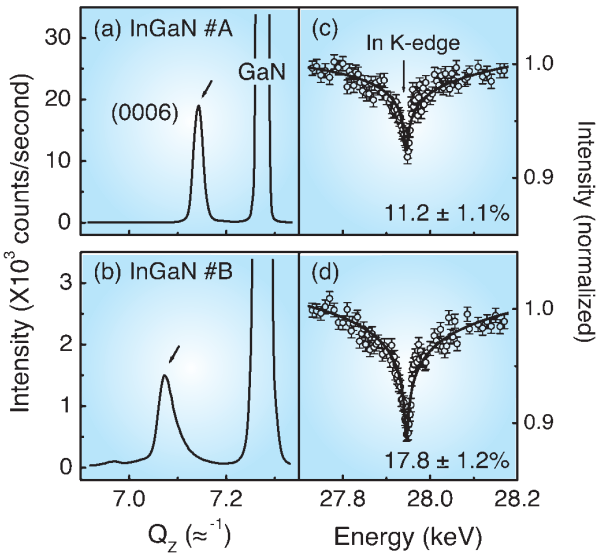

Fig. 1: (a, b) InGaN (0006) diffraction profiles of the InGaN films. (c, d) Normalized AXS spectra of InGaN films measured at the (0006) Bragg peak position across indium K-edge. Solid lines are fits.

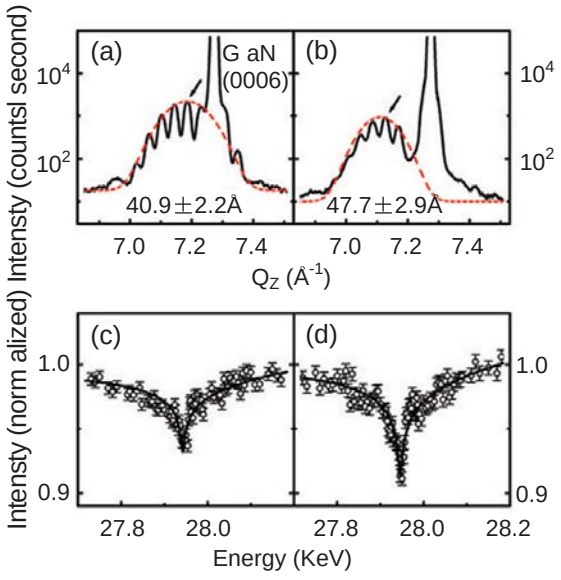

Fig. 2: (a, b) profile of MQWs near the (0006) peak. Dotted lines represent the structure factor of the InGaN well layers. (c, d) Normalized AXS spectra of MQWs measured at the superlattice peak by the arrows. Solid lines are the fits.

where *MLF* is a multi-layer factor for an N-period superlattice, S_{InGaN} (S_{GaN}) is the structure factor of the well (barrier), and the stack period Λ is the thickness of single InGaN/GaN well-barrier pair. The broad envelope feature near 7.15 $Å^{-1}$ shown in Fig. 2(a) and 2(b) represents the InGaN well structure factor, S_{InGaN} . The dotted lines represent fits to a Gaussian describing the InGaN form factor. The d_{InGaN} of MQW #A (#B) obtained from the fits is 40.9±2.2 Å (47.7±2.9 Å). The sharp peaks riding on the envelope are the superlattice peaks centered at integer multiples of $2\pi/\Lambda$. The peak position is completely determined by the stack period, Λ and independent of the indium composition. Estimating the In composition from the superlattice peak position rather than from the peak of the broad envelope is a common mistake that one can make.

For the composition analysis, we measured the AXS spectra, shown in Fig. 2(c) and 2(d) at the strongest superlattice peak indicated by arrows depicted in the figures. Although the diffraction from the InGaN well layer is far from that of the GaN barrier layer, it is essential to subtract the tail of the GaN peak before the composition analysis. Different from the case of thick InGaN films, the contribution from the GaN barriers is significant even at the InGaN (0006). Rearranging Eq. (2), we obtain,

$$I_{InGaN} = |S_{InGaN}|^2 = \left(\sqrt{I_M - |S_{GaN}|^2 \sin^2\phi} - |S_{GaN}| \cdot \cos\phi\right)^2, \quad (3)$$

where I_M is the measured intensity and ϕ is the relative phase between the structure factor of the wells and the barriers. S_{GaN} and ϕ are obtained by fitting the XRD profile. For the structural and compositional analysis of multi-layer thin films, therefore, a combined analysis of AXS and XRD is necessary. Analyzing the energy dependence of the calculated I_{nGaN} intensity, given by Eq. (3), we obtain the indium composition of MQW #A = 12.8% and of MQW #B = 15.1%. These values are comparable to those of the InGaN thin films grown under similar conditions.

In summary, we have determined the absolute indium content incorporated in the crystalline lattice of InGaN films and InGaN/GaN MQWs using AXS measurement. The resolution in the composition analysis using AXS was about 1%. In the case of the MQWs it was essential to analyze the AXS spectra and the XRD pattern simultaneously at a higher order (0006) Bragg reflection.

Beamline:

SP12B1 Materials X-ray Study beamline

Experimental Station:

X-ray scattering end station

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