# Composition determination of β-$(Al_xGa_{1-x})_2O_3$ layers coherently grown on (010) β-$Ga_2O_3$ substrates by high-resolution x-ray diffraction

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We demonstrate x-ray diffraction based composition estimation of β-$(Al_xGa_{1-x})_2O_3$ coherently grown on (010) β-$Ga_2O_3$. The relation between the strain along the [010] direction and the Al composition of the β-$(Al_xGa_{1-x})_2O_3$ layer was formulated by using stress-strain relationship in the monoclinic system. This formulation allows us to estimate the Al composition using out-of-plane lattice spacing determined by conventional x-ray $\omega$-$2\theta$ measurements. This method was applied to MBE-grown coherent β-$(Al_xGa_{1-x})_2O_3$/$Ga_2O_3$ heterostructures, and the Al composition in the β-$(Al_xGa_{1-x})_2O_3$ are in close agreement with composition determined directly by atom probe tomography.

β-$Ga_2O_3$ is a wide bandgap semiconductor ($E_g$ = 4.7 - 4.9 eV),[1-3] which crystalizes in the monoclinic structure. β-$Ga_2O_3$ is attracting a remarkable attention due to its great potential to realize power devices with higher breakdown voltages and lower energy losses than its counterparts GaN and SiC. In reality, several promising results have already been reported on β-$Ga_2O_3$ based power devices such as Schottky barrier diodes,[4] metal-semiconductor field effect transistors (MESFETs),[5] and metal-oxide field effect transistors (MOSFETs).[6] In addition, β-$(Al_xGa_{1-x})_2O_3$ solid solutions and β-$(Al_xGa_{1-x})_2O_3$/β-$Ga_2O_3$ hetero-structures have been studied intensively since these will enable band engineering and lead to the realization of further high-performance β-$Ga_2O_3$ based devices such as high electron mobility transistors (HEMTs).[7,8]

$Ga_2O_3$ and $Al_2O_3$ crystalize in different crystal structures, *i.e.*, the β-gallia structure and the corundum structure, respectively. They therefore make solid solutions β-$(Al_xGa_{1-x})_2O_3$ under certain solubility limit $x_{max}$. Hill *et al*. investigated the equilibrium phase diagram of $Al_2O_3$-$Ga_2O_3$ system by using powder synthesis technique and reported the lattice parameters of β-$(Al_xGa_{1-x})_2O_3$.[9] The phase diagram shows that $x_{max}$ increases with temperature. For example, $x_{max}$ is more than 0.6 at 800°C or higher, while $x_{max}$ is about 0.25 at 650°C, which is the growth temperature of molecular beam epitaxy (MBE) in the present work. Recently, Karnert *et al*. investigated the lattice parameters of their β-$(Al_xGa_{1-x})_2O_3$ ceramics.[10] The lattice parameters exhibited linear dependence on $x$ when $x$ is 0.3 or lower regardless of the sintering temperature.

A prompt and non-destructive composition measurement is essential in materials development. In the case of relaxed β-$(Al_xGa_{1-x})_2O_3$, the Al composition can be determined immediately through lattice parameters measurement by x-ray diffraction (XRD). However, the Al composition of strained β-$(Al_xGa_{1-x})_2O_3$ cannot be estimated directly through lattice parameters measurement since the crystal lattice is elastically deformed and the lattice parameters are different from the relaxed values.

There are a few reports on the estimation of Al composition of strained β-$(Al_xGa_{1-x})_2O_3$. Oshima *et al*. utilized x-ray photoelectron spectroscopy (XPS) to estimate the Al composition of their films coherently grown on (100) β-$Ga_2O_3$ substrates by MBE.[7] However, XPS can collect the data only from the outermost surface (typically a few nanometers deep). Therefore, the measurement can be disturbed when the surface composition is different from that of the body layer. Kaun *et al*. utilized transmission electron microscopy and energy dispersive X-ray spectroscopy (TEM-EDS) to estimate the

Al composition of β-$(Al_xGa_{1-x})_2O_3$ coherently grown on (010) β-$Ga_2O_3$ by MBE.[8] However, the measurement is destructive and time-consuming.

In an analogous case of $Al_xGa_{1-x}N$, Al composition of a coherently grown film has been estimated from the out-of-plane lattice spacing with considering the Poisson effect.[11] In the present work, we demonstrate a quick and non-destructive estimation of Al composition of coherently grown (010) β-$(Al_xGa_{1-x})_2O_3$ films using a methodology similar to the case of $Al_xGa_{1-x}N$.

First, we formulate the relation between the Al composition and the strain along [010]. In the following calculations, the β-$(Al_xGa_{1-x})_2O_3$ layer is assumed to be grown coherently. The unit cells is placed in the Cartesian system so that [100] || $\hat{x}_1$ and [010] || $\hat{x}_2$, where $\hat{x}_1$ and $\hat{x}_2$ are the Cartesian unit vectors. We used standard matrix notation to express elastic stiffness tensor $\boldsymbol{c}$, stress tensor $\boldsymbol{\sigma}$, and strain tensor $\boldsymbol{\varepsilon}$. The notation rule can be found in Ref. 12, for example. When β-$(Al_xGa_{1-x})_2O_3$ is grown on (010) β-$Ga_2O_3$ coherently, β-$(Al_xGa_{1-x})_2O_3$ is subjected to in-plane biaxial stress. Accordingly, only in-plane stress components have non-zero values. Similarly, the shear strain $\varepsilon_4$ and $\varepsilon_6$ are zero . Therefore, stress-strain relation in a coherently grown (010) β-$(Al_xGa_{1-x})_2O_3$ film is expressed as follows:

$$\begin{bmatrix} \sigma_1 \\ 0 \\ \sigma_3 \\ 0 \\ \sigma_5 \\ 0 \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & c_{15} & 0 \\ c_{12} & c_{22} & c_{23} & 0 & c_{25} & 0 \\ c_{13} & c_{23} & c_{33} & 0 & c_{35} & 0 \\ 0 & 0 & 0 & c_{44} & 0 & c_{46} \\ c_{15} & c_{25} & c_{35} & 0 & c_{55} & 0 \\ 0 & 0 & 0 & c_{46} & 0 & c_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ 0 \\ \varepsilon_5 \\ 0 \end{bmatrix} \qquad (1)$$

From the second line in eq. (1), we obtain the following relationship:

$$\varepsilon_2 = -\frac{c_{12}\varepsilon_1 + c_{23}\varepsilon_3 + c_{25}\varepsilon_5}{c_{22}} \qquad (2)$$

When the crystal lattice of β-$(Al_xGa_{1-x})_2O_3$ deforms elastically so as to fit that of β-$Ga_2O_3$, strain components in eq. (2) are given as:

$$\varepsilon_1 = \frac{a_c - a_r}{a_r} \quad (3a)$$

$$\varepsilon_3 = \frac{c_c sin\beta_c}{c_r sin\beta_r} - 1 \quad (3b)$$

$$\varepsilon_5 = \frac{c_c cos\beta_c}{c_r sin\beta_r} - \frac{a_c cos\beta_r}{a_r sin\beta_r} \quad (3c)$$

Here, $a_c$, $c_c$, $\beta_c$ are the in-plane lattice parameters of coherently grown β-$(Al_xGa_{1-x})_2O_3$, which coincide with those of β-$Ga_2O_3$ ($a_0$ = 12.21 Å, $b_0$ = 3.04 Å, $c_0$ = 5.81 Å, $\beta_0$ = 103.87°).[10] $a_r$, $c_r$, $\beta_r$ are the in-plane lattice parameters of relaxed β-$(Al_xGa_{1-x})_2O_3$. Kranert *et al.*[10] have reported these values as functions of $x$:

$$a_r = a_0 - k_a x \text{ [Å]} \quad (4a)$$

$$b_r = b_0 - k_b x \text{ [Å]} \quad (4b)$$

$$c_r = c_0 - k_c x \text{ [Å]} \quad (4c)$$

$$\beta_r = \beta_0 + k_\beta x \text{ [deg.]} \quad (4d)$$

Here, $k_a$ = 0.42, $k_b$ = 0.13, $k_c$ = 0.17, and $k_\beta$ = 0.31. On the other hand, $\varepsilon_2$ can also be expressed as follows:

$$\varepsilon_2 = -\frac{b_r - b_c}{b_r} \quad (5)$$

$b_c$ is the length of $b$-axis of coherently grown β-$(Al_xGa_{1-x})_2O_3$, which can be experimentally determined through XRD $\omega$-$2\theta$ measurement. We can determine $x$ by equating eqs. (2) and (5), and solving the equation for $x$ with using eqs. (3a)~(3c) and (4a)~(4d). The result is as follows:

$$x \cong \frac{b_0 - b_c}{b_0} \cdot \left[\frac{k_b}{b_0} + \frac{c_{12}}{c_{22}} \cdot \frac{k_a}{a_0} + \frac{c_{23}}{c_{22}} \cdot \frac{k_c}{c_0} + \frac{c_{25}}{c_{22}}\left(\frac{k_c}{c_0} - \frac{k_a}{a_0}\right) cot\beta_0\right]^{-1} \quad (6a)$$

Eq. (6a) is also expressed as follows by using on-axis peak separation of the film and the substrate $\Delta\theta$, and substrate peak position $\theta_0$:

$$x \cong \Delta\theta cot\theta_0 \cdot \left[\frac{k_b}{b_0} + \frac{c_{12}}{c_{22}} \cdot \frac{k_a}{a_0} + \frac{c_{23}}{c_{22}} \cdot \frac{k_c}{c_0} + \frac{c_{25}}{c_{22}}\left(\frac{k_c}{c_0} - \frac{k_a}{a_0}\right) cot\beta_0\right]^{-1} \qquad (6b)$$

To the best of our knowledge, no experimental elastic stiffness tensor is reported about β-$(Al_xGa_{1-x})_2O_3$. We therefore used a result of first-principles calculation for β-$Ga_2O_3$. In general, elastic stiffness components show only a slight variation by alloying with small molar fraction, and they tend to vary toward the same direction. Therefore, the variation of their ratio is virtually negligible. The use of elastic stiffness of β-$Ga_2O_3$ is therefore a good approximation since elastic stiffness components appear as their ratio in eq. (2). The calculation was carried out using the projector augmented wave (PAW) method[13] under local density approximation (LDA) in the Vienna Ab-Inition Simulation Package (VASP).[14] We used a plane-wave basis set with an energy cutoff $E_{cut}$ = 500 eV and a 2 × 4 × 8 k-point grid. Elastic constants were calculated with the strain-stress method based on the set of six universal deformation modes proposed in ref. 15. The following result was employed in the composition estimation.

$$\begin{bmatrix} 237 & 125 & 147 & 0 & -18 & 0 \\ 125 & 354 & 95 & 0 & 11 & 0 \\ 147 & 95 & 357 & 0 & 6 & 0 \\ 0 & 0 & 0 & 54 & 0 & 19 \\ -18 & 11 & 6 & 0 & 67 & 0 \\ 0 & 0 & 0 & 19 & 0 & 95 \end{bmatrix} \text{[GPa]} \qquad (7)$$

Finally, eqs. (6a) is written as:

$$x \cong 15.923 - 5.238 \times b_c[\text{Å}] \qquad (8a)$$

When *020* diffraction is used, eq. (6b) is written as:

$$x \cong 0.4727 \times \Delta\theta_{020} \qquad (8b)$$

To examine the methodology described above, we compared the Al compositions estimated by this new method and those measured directly by pulsed laser atom probe tomography (APT).[16,17] The β-$(Al_xGa_{1-x})_2O_3$ films were grown on (010) β-$Ga_2O_3$ single crystal substrates at 650°C by plasma-assisted MBE. Two different samples were prepared with beam flux ratio $\phi_{Al}$ / ($\phi_{Al}$ + $\phi_{Ga}$) = 0.061 and 0.104. The detail of the growth is described

elsewhere.[8,18] High-resolution x-ray diffraction measurements were performed in a triple axis configuration using $CuK_\alpha$ radiation ($\lambda$ = 1.5406 Å) at room temperature. Out-of-plane lattice spacing of each film was directly determined through symmetrical $\omega$-$2\theta$ measurement using *020* diffraction. Asymmetrical reciprocal lattice mapping (RSM) using *420* diffraction was carried out to confirm the coherent growth. After the XRD measurements, a 200-nm-thick β-$Ga_2O_3$ capping layer was additionally grown by MBE on each β-$(Al_xGa_{1-x})_2O_3$ layer before producing a tip sample for APT to ensure that the whole thickness of the β-$(Al_xGa_{1-x})_2O_3$ layer was included in the tip. APT samples were prepared by focus ion beam (FIB) technique. About 150 nm wide needle like tips were polished using a FEI Helios Dual Beam Nanolab 650 instrument, milled at 30 kV and followed by a final cleaning at 5 kV. The experiment was carried out using a Cameca LEAP 3000X atom probe instrument equipped with a 532 nm green pulsed laser. The laser energy is around 0.2 nJ, the tip temperature was about 40K and evaporation rate was 1%.

Figures 1(a) and (b) show the XRD $\omega$-$2\theta$ profiles of the β-$(Al_xGa_{1-x})_2O_3$ films. Each profile exhibited a single β-$(Al_xGa_{1-x})_2O_3$ *020* diffraction peak with thickness fringes. The out-of-plane lattice spacing of the films were determined to be (a) 3.019 Å and (b) 3.009 Å, respectively. The thicknesses of the two films determined from the fringe spacing were 130 and 127 nm, respectively.

Figure 2(a) and (b) show the RSMs of the two films. The *420* peaks of β-$Ga_2O_3$ and β-$(Al_xGa_{1-x})_2O_3$ appeared at the same $q_x$ position in each RSM, indicating that the β-$(Al_xGa_{1-x})_2O_3$ films were grown coherently.

Figure 3(a) and (b) show the depth profiles of the Al and Ga compositions for the two films measured by APT. The film composition was nearly uniform along the growth direction of the β-$(Al_xGa_{1-x})_2O_3$ films. The average Al composition in each film was 0.120 and 0.168. These values are significantly higher than those expected from the beam flux ratio. This is probably due to the low incorporation efficiency of Ga because of the formation of volatile suboxide $Ga_2O$.[12,19]

The calculated Al composition of coherently grown β-$(Al_xGa_{1-x})_2O_3$ is shown in Fig. 4 as a function of $b_c$ together with the averaged APT results. We also show the relationship for relaxed β-$(Al_xGa_{1-x})_2O_3$ reported by Kranert *et al.*[10] for comparison. The calculated result for coherent films is in good agreement with the APT results, while the application of the relaxed line to the fully strained films results in significant overestimation.

In summary, the Al composition of β-$(Al_xGa_{1-x})_2O_3$ films coherently grown on (010)

β-$Ga_2O_3$ by MBE was successfully estimated by conventional XRD $\omega$-$2\theta$ measurement with considering the Poisson effect in the monoclinic system. Coherent growth was confirmed by RSM measurement. The elastic stiffness tensor of β-$Ga_2O_3$ obtained by first-principle calculation was utilized in the estimation. The result was in a close agreement with the Al compositions directly measured by APT. This methodology enables us to estimate the Al composition of coherently grown β-$(Al_xGa_{1-x})_2O_3$ in a rapid and non-destructive manner, and thus it will boost the development of high-performance β-$Ga_2O_3$ based devices.

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## Figure Captions

**Fig. 1.** XRD $\omega$-$2\theta$ scan profiles of β-$(Al_xGa_{1-x})_2O_3$ films. (a) $\phi_{Al} / (\phi_{Al} + \phi_{Ga})$ = 0.061, (b) $\phi_{Al} / (\phi_{Al} + \phi_{Ga})$ = 0.104.

**Fig. 2.** RSMs of β-$(Al_xGa_{1-x})_2O_3$ films. (a) $\phi_{Al} / (\phi_{Al} + \phi_{Ga})$ = 0.061, (b) $\phi_{Al} / (\phi_{Al} + \phi_{Ga})$ = 0.104.

**Fig. 3.** Depth profiles of Al and Ga compositions of β-$(Al_xGa_{1-x})_2O_3$ films measured by APT. (a) $\phi_{Al} / (\phi_{Al} + \phi_{Ga})$ = 0.061, (b) $\phi_{Al} / (\phi_{Al} + \phi_{Ga})$ = 0.104.

**Fig. 4.** Relationships between $b_c$ and Al composition $x$. Error bars show ±2σ. The calculated result for coherent films is approximated by eq. (8a).

## Figures

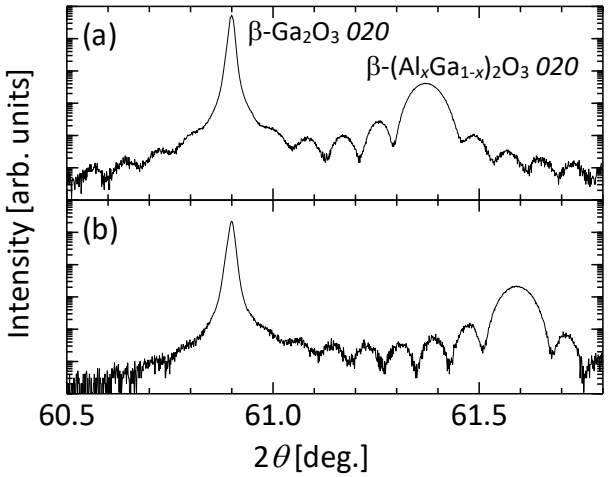


Fig. 1.

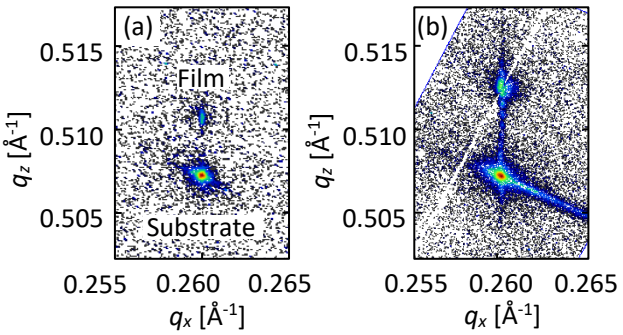


Fig. 2.

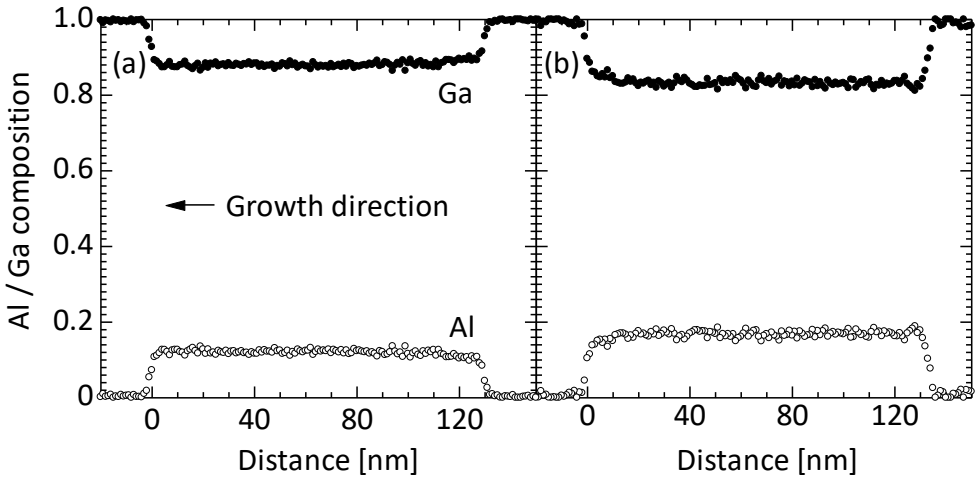
1.0
0.8
0.6
0.4
0.2
0
Al / Ga composition
(a)
(b)
Ga
Growth direction
Al
0
40
80
120
Distance [nm]

Fig. 3.

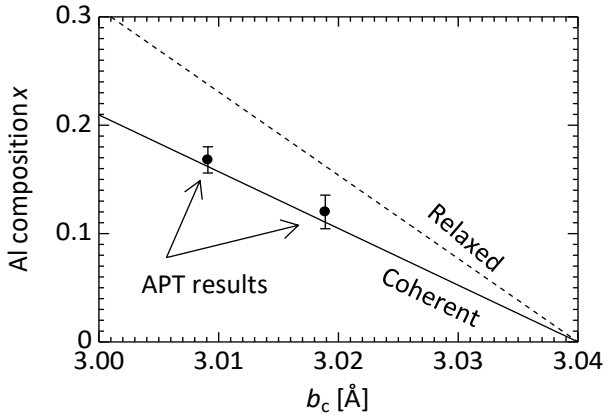
0.3
0.2
0.1
0
Al composition x
Relaxed
Coherent
APT results
3.00
3.01
3.02
3.03
3.04
$b_c$ [Å]

Fig. 4.