Influence of growth rate and temperature on InP/GaInAs interface structure analyzed by X-ray CTR Scattering measurement

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Abstract

Most of high performance III-V compound semiconductor devices are fabricated utilizing heterostructures. However, when the heterostructures are grown by OMVPE, a compositional grading arises at a hetero-interfaces. The compositional grading may deteriorate the performance of the compound semiconductor devices. We have investigated the degree of the compositional grading at the interfaces using X-ray crystal truncation rod (CTR) scattering measurement. The X-ray CTR scattering measurement is a powerful technique to investigate the buried interfaces and determine the distributions of atoms quantitatively at an atomic-scale. In this work, we studied on the distributions of group-III atoms at InP/GaInAs interfaces grown by OMVPE with different growth rates, focusing on the influence of the exchange reaction of the group-III atoms near the surface during the growing. The experimental results showed that the degree of distributions of Ga atoms increased with the decrease of the growth rate. It suggested that the distribution of Ga atoms at interfaces were influenced by the exchange reaction. In order to discuss the exchange reaction, a calculation to simulate the distribution of Ga atoms was conducted considering potential energy of Ga in InP layers. The results showed that Ga atoms should exchange during the growth in top-most 3 atomic layers.

I. Background

Heterostructures of III-V compound semiconductors are utilized for high performance devices, such as, HEMTs (high electron mobility transistors), lasers, and HBTs (heterojunction-bipolar transistors). Nowadays, such high performance devices are designed at an atomic-scale. However, even when the heterostructures are grown by OMVPE (organometallic vapor phase epitaxy), which is one of the most advanced crystal growth technique, a compositional grading arises unexpectedly at the heterointerfaces. When the devices are designed at an atomic-scale, the compositional grading cannot be ignored since it causes deterioration of device performances. We have investigated the degree of the compositional grading at the interfaces using X-ray crystal truncation rod (CTR) scattering measurement and shown that the group-V atoms and the group-III atoms are not distributed in the structure as designed. CTR scattering is an X-ray intensity distribution caused by the truncation of periodicity of a crystal at a surface. The X-ray CTR scattering measurement is a very powerful technique to analyze the interface structures in hetero-epitaxially grown III-V compound semiconductors at an atomic-scale. The X-ray CTR scattering measurement can reveal layer thicknesses, distributions of atoms, surface roughness, and lattice constants.

In the previous works, it was shown that the compositional grading of group-V atoms at InP/GaInAs interfaces can be suppressed by controlling H_2-flushing time after the growth of the GaInAs layer. The result suggested that the compositional grading of group-V atoms is mainly caused by the adsorption of As on the surface. In contrast, the H_2-flushing time did not influence the compositional grading of group-III atoms. Therefore, there must be other effects that cause the compositional grading of group-III atoms.

In this work, we focused on the change of the compositional grading of group-III atoms at InP/GaInAs interface with the change of the growth rate to study the exchange reaction of the group-III atoms near the surface during the growth. If the exchange reaction has any contribution on the compositional grading of the group-III atoms, the degree of the Ga distribution in the InP cap layer should increase with the decrease of the growth rate since the opportunity of the exchange should increase when the growth rate is low, and it takes a longer time to form 1 atomic layer.

II. Experimental

The InP(10nm)/$Ga_{0.47}In_{0.53}As$(15ML)/InP structure samples were grown by OMVPE with a vertical reactor. The pressure in the reactor during the growth was kept at 76.0 Torr. Precursors were triethylgallium (TEGa), trimethylindium (TMIn), tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP). Hydrogen was used as a carrier gas, and the total flow rate of the hydrogen was kept at the same for all the samples. Exactly (001) oriented InP substrates were used for the growth. The growth rate was varied from 0.1 to 1.0 ML/s by changing the flow rates of the group-III precursors keeping the V/III ratio at 20, and the growth temperature was 590, 620, or 650°C.

The X-ray CTR scattering measurement was carried out at the BL6A of the Photon Factory in the High Energy Accelerator Research Organization at Tsukuba. Wavelength of the X-ray was set at 0.1nm. A CCD camera was used to record the distribution of the scattered X-ray intensity around a Bragg peak.

For example, measured X-ray CTR scattering spectra of the InP/$Ga_{0.47}In_{0.53}As$/InP structure samples grown at 590°C are shown in Fig. 1. The spectra were measured along [00ℓ] direction in the reciprocal space. The direction was normal to the surfaces of the samples. The peaks observed at ℓ=2 are 002 Bragg peak of InP, although they were not plotted near the Bragg point since the peaks were too high. As shown in Fig. 1, clear oscillations were observed in the range of $1.6 < \ell < 2.4$ for all the samples. The oscillation was caused by the interferences between reflected X-ray by InP and GaInAs layers.

The X-ray CTR scattering spectra were analyzed by comparing them with theoretically calculated spectra based on a model structure as shown in Fig. 2. The compositional grading of Ga and As were assumed to be represented as

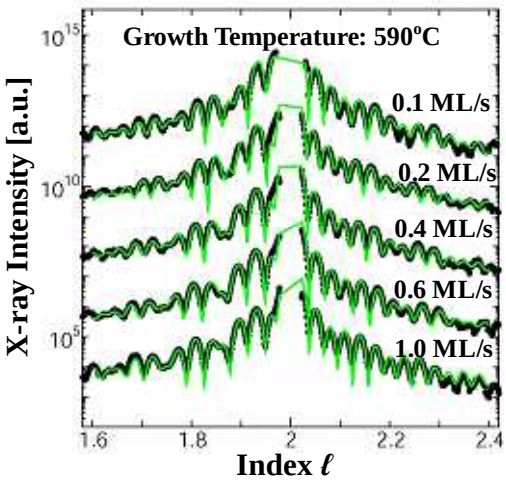


Fig. 1: Measured and theoretically calculated X-ray CTR scattering spectra. The peaks at ℓ=2.0, which were InP 002 Bragg peaks, were not plotted since the X-ray intensity was too strong.

$$x(n) = x_h \exp\left(-\frac{n}{d}\right)$$

where $x(n)$ is a composition of Ga or As in a layer n [ML] away from a interface, x_h is peak composition, and d indicates degree of compositional grading. The theoretically calculated best-fitted spectra are also shown in Fig. 1 as grey lines.

III. Results and Discussion

Figure 3 shows the relationship between the growth rate and the amount of Ga distributed in the InP cap layer obtained from the analysis of the CTR scattering spectra. As shown in Fig. 3, the amount of Ga increased with the decrease of the growth rate. It suggested that the exchange reaction contributed to the Ga distribution in InP on the GaInAs layer. The exchange reaction can be discussed from the change of the Ga distributions depending on the growth rate and temperature.

Figure 4 shows a schematic potential energy diagram of Ga atom in InP. The diagram includes energy levels of metastable sites, D_i, barrier height of the exchange process, E_b, and activation energy for the desorption from surface, E_d, where i is number of molecular layer. The Ga distributions were simulated described as follows based on the

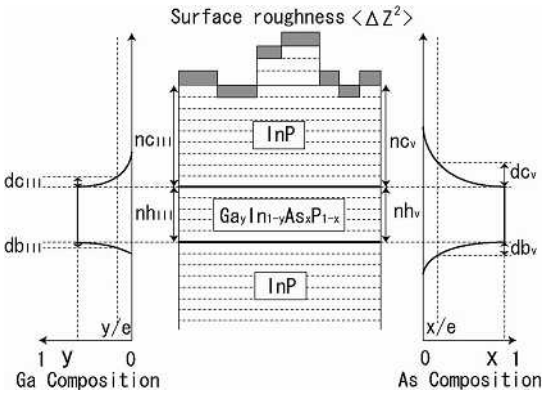
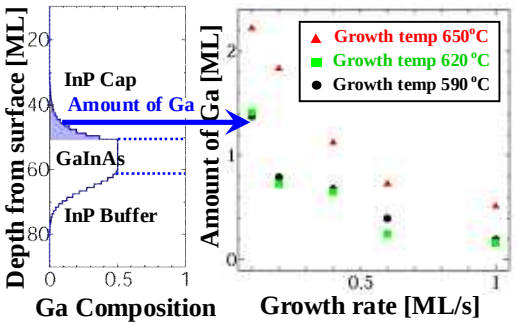


Fig. 2. A model structure to calculate a CTR scattering spectrum. The measured X-ray CTR scattering spectra were analyzed by comparing them with the theoretically calculated spectra based on this model. The model structure containes 10 parameters to describe the distributions of Ga and As in the InP/GaInAs/InP hetero-structure.



(a) (b)

Fig. 3 : (a) An example of the measured Ga distribution in InP/GaInAs/InP structure obtained from the analysis of a CTR scattering spectum. In this work, the change of the amount of Ga in InP cap layer (in hatched region) is discussed. (b) Measured relationships between amount of Ga and growth rate at different growth temperature.

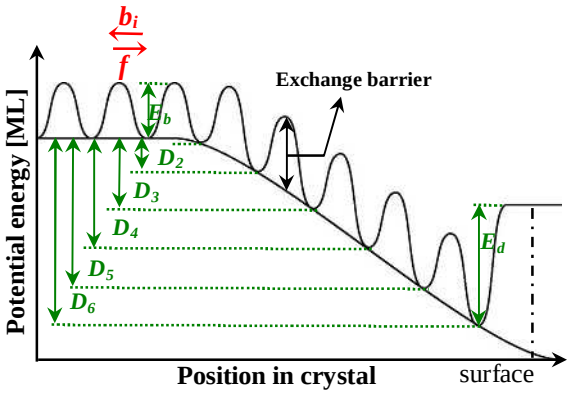


Fig. 4: Schematic potential energy diagram of Ga atoms in InP to describe exchange processes. Ga atoms at valley states exchange through barriers. The exchange rate from surface to inside, b_i, and inside to surface, f, could be different.

diagram and the simulated distributions were compared with the measured ones to find a set of the parameters, D_i, E_b and E_d, which represents the measured distributions well. Using the parameters, the exchange rate from inside to surface, f, the exchange rate from surface to inside, b_i, and the distribution rate, d, are defined as

$$b_i = \upsilon \exp\left\{-\frac{E_b + (D_i - D_{i-1})}{k_B T}\right\} \quad (1)$$

$$f = \upsilon \exp\left\{-\frac{E_b}{k_B T}\right\} \quad (2)$$

$$d = \upsilon \exp\left\{-\frac{E_d}{k_B T}\right\} \quad (3)$$

where k_B and T are Boltzman constant and the growth temperature, respectively. υ is a "successful-attempt" frequency. As shown in Fig. 4, the energy levels of two metastable sites next to a barrier could be different. Therefore, the exchange rate from inside to surface, f, and from surface to inside, b_i, could be different. The compositions of Ga atom in the growing layer were obtained step by step by calculating the following iteration equations.

$$\begin{cases} C_n^1 = \int_0^{t_m} (fC_{n-1}^2 - b_6 C_{n-1}^1 - dC_{n-1}^1)dt \\ C_n^2 = \int_0^{t_m} (fC_{n-1}^3 - b_5 C_{n-1}^2 + b_6 C_{n-1}^1 - fC_{n-1}^2)dt \\ C_n^3 = \int_0^{t_m} (fC_{n-1}^4 - b_4 C_{n-1}^3 + b_5 C_{n-1}^2 - fC_{n-1}^3)dt \\ C_n^4 = \int_0^{t_m} (fC_{n-1}^5 - b_3 C_{n-1}^4 + b_4 C_{n-1}^3 - fC_{n-1}^4)dt \\ C_n^5 = \int_0^{t_m} (fC_{n-1}^6 - b_2 C_{n-1}^5 + b_3 C_{n-1}^4 - fC_{n-1}^5)dt \\ C_n^6 = \int_0^{t_m} (fC_{n-1}^7 - b_1 C_{n-1}^6 + b_2 C_{n-1}^5 - fC_{n-1}^6)dt \\ C_n^7 = \int_0^{t_m} (b_1 C_{n-1}^6 - fC_{n-1}^7)dt \end{cases} \quad (4)$$

n is the iteration step. C_n^L is a Ga composition L [ML] away from the surface and $n \times t_m$ [sec] later from the start of the growth. $t_m = 1/G$ is a time to form 1 atomic layer, where G is a growth rate. As shown in the equations, the Ga composition, C_n^L, is determined from the compositions at t_m earlier considering the exchange of atoms (f and b_i) and desorption from surface (d). It was assumed that Ga composition was 0.47 in all the layers, initially, and that the Ga atoms in only top-most 6 layers can exchange.

Table I: Potential energys and exchange rates which represented the Ga distributions best matched to the measured ones as shown in Fig. 5.

D_1	D_2	D_3	D_4	D_5	D_6	E_b	E_d
0.080eV	0.080eV	0.080eV	1.8eV	3.2eV	3.2eV	1.4eV	2.0eV

	b_1	b_2	b_3	b_4	b_5	b_6	f	d
650℃	0.057	0.16	0.16	5.4×10^{-11}	0.34×10^{-9}	0.043	0.16	8.2×10^{-5}
620℃	0.030	0.084	0.084	1.4×10^{-11}	1.2×10^{-9}	0.084	0.084	3.4×10^{-5}
590℃	0.015	0.043	0.043	0.33×10^{-11}	4.1×10^{-9}	0.16	0.043	1.3×10^{-5}

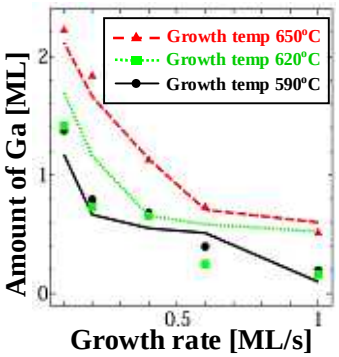


Fig. 5: Comparison between the measured amounts of Ga and simulated ones.

Figure 5 shows finally obtained relationships between the amount of Ga and growth rate at all the temperatures, 590, 620 and 650°C. All the results shown in Fig. 5 were calculated from one set of the parameters listed in Table I. Only the growth temperature and the growth rate were changed for the different calculated points. The potential energy diagram drawn with the parameters is shown in Fig. 6. As shown in Fig. 6, in order to explain the observed Ga distributions, the exchange should occur mainly in top-most 3 molecular layers during the growth. The barrier heights, about 1.4eV, corresponded to the energy to break 1 or 2 bonds. The energy levels of the metastable sites in the top-most 3 molecular layers decreased by about 1.8 and 3eV from the metastable sites located far from the surface. The result suggested that Ga atoms in top-most 3 layers were weakly bonding with only 1 or 2 bonds during the growth.

IV. Conclusions

We have investigated, using X-ray CTR scattering measurements, the influence of the growth rate and the temperature on InP/GaInAs interface structures grown by OMVPE changing growth rate and growth temperature.

The experimental results showed that the degree of the Ga distribution in the InP cap layer was small at higher growth rate. In order to discuss the exchange reaction, a calculation was conducted to obtain the distribution of Ga atoms considering potential energy of Ga in InP layers. The

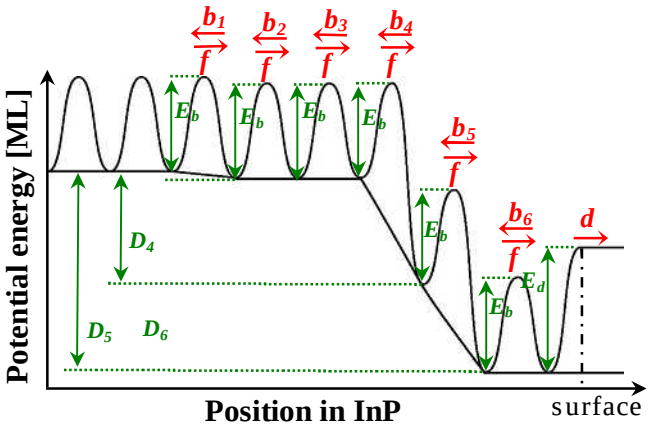


Fig. 6: Schematic potential energy diagram drawn with the parameters listed in table I.

calculation successfully represented the distributions of Ga in the samples grown at different growth rate and temperature from only a set of potential energies. The results showed that Ga atoms should exchange during the growth in top-most 3 atomic layers

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