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Study on Buried Interfaces in Semiconductor Heterostructures by X-ray Reflectivity

Yoshikazu Takeda and Masao Tabuchi*
Department of Crystalline Materials Science, Graduate School of Engineering
Nagoya University
Nagoya 464-8603, Japan
Fax: 81-52-789-3239, e-mail: takeda@numse.nagoya-u.ac.jp
*Venture Business Laboratory
Nagoya University
Nagoya 464-8603, Japan
Fax: 81-52-789-5442, e-mail: tabuchi@vbl.nagoya-u.ac.jp

X-ray reflectivity around the Bragg point has been applied to reveal the heterostructures and interfaces of many semiconductor materials combinations. We started with a simple structure of As δ-doping to test the capability of the technique to reveal the structure of a buried sub-monolayer, where the crystal structure is not changed and the model is simple. It was extended to realistic structures, *i.e.*, single quantum well with different materials combinations such as InP/GaInAs/InP, InP/ErP/InP, and ZnSe/GaAs. It is demonstrated, using GaInP/GaAs/GaInP double heterostructures as an example, that this technique is a very powerful tool to correlate the growth process and the device properties through atomistic elucidation of the buried heterostructures nondestructively.
Key words: X-ray, reflectivity, Bragg point, buried heterostructures, device properties, growth process

1. INTRODUCTION

Measurement of X-ray reflectivity around the Bragg point gives X-ray CTR (Crystal Truncation Rod) [1,2]. It is so called because the measured X-ray intensity distribution looks like a "rod" caused by the termination of the periodicity (*i.e.*, the surface) of a crystal. CTR may be used hereafter since it is short to express. We have used this CTR extensively to analyze buried heterostructures since the rod (reflectivity) is largely modified not only due to the surface structures but also due to the layer structures underneath the surface.

The interests to us, crystal growers and device researchers, are a nondestructive and *ex-situ* measurements of the heterostructure (a basic part of device structures) where carriers run and recombine under the device operations.

In the MBE (molecular beam epitaxy) we have an electron beam (RHEED) as a tool to observe the surface structure in the atomistic level. However, the active layer is capped to form heterostructures and we do not know what happened during and after the capping. In the MOVPE (metalorganic vapor phase epitaxy), optical measurements (reflectivity and ellipsometry) are often used. Those techniques are also sensitive to the top surface of the growing crystal.

TEM (transmission electron microscopy) is a powerful technique to investigate the atomistic structure of materials. However, the inevitable process of thinning often causes unpredictable damages and modification of the structures. In the strained layers, the strain is released due to the thinning and the real buried structure disappears.

Thus, the nondestructive and atomistic measurements and analyses are very important to understand what the real structure is, what the relationship between structures and device properties is, and then to control the heterostructures.

We have applied the X-ray CTR scattering measurement technique to analyze:

1) As/P atom exchange process at AsH_3-exposed and/or PH_3-exposed InP surface [3,4],
2) Composition profiles of InP/(InAsP or GaInAs)/InP heterostructures grown by difference MOVPE processes [5-9],
3) Composition profiles and crystal structure of ErP in InP/ErP/InP heterostructures [10-12],
4) Thermal diffusion processes of In in GaAs/InAs (1ML)/GaAs and Er in InP/ErP(δ-doped)/InP [13,14],
5) Heterointerface structures of ZnSe on GaAs under different pre-treatments of the GaAs surface [15],
6) Characterization of nitrided sapphire surfaces for GaN growth [16],
7) Characterization of low-temperature-deposited (LT) AlN for GaN growth [17,18],
8) Characterization of whole structure of GaInN/GaN/LT-AlN/sapphire [19,20],

and many others [21-25].

In this paper we demonstrate a clear relationship between atom distribution and device properties, which was revealed, after several peripheral experiments, by the X-ray CTR scattering measurements as a final and definitive experiment. This paper is an extended version of Ref. 26.

2. BROAD EMISSION FROM GaInP/GaAs/GaInP

GaInP/GaAs/GaInP double heterostructure (DH) is used for lasers in the near infrared region and heterojunction bipolar transistors (HBT) for high frequency power transistors.

We were growing, by MOVPE, GaInP/GaAs/GaInP double heterostructures to dope the GaAs well layer with Er and O for light emission at 1.54 μm [27]. In this material combination, a broad and quite intensive emission at around 0.95μm was a problem to be solved.

2.1 Growth temperature dependence

Figure 1 (a) shows photoluminescence (PL) spectra from GaInP/GaAs/GaInP heterostructures grown at different temperatures. When the whole layer was grown at 610°C that was the best growth temperature for GaAs, a broad emission at around 950 nm predominated (top figure). The band-edge emission from GaAs is 820 nm and that of GaInP is 640nm at 77K. Since PL from a single layer GaInP and GaAs grown respectively at 610°C and 550°C showed only the band-edge emission from each layer, this broad emission should come from near the interface. But it was suppressed at a lower growth temperature as shown in Fig. 1 (a) bottom. 550°C was the best growth temperature to obtain the highest PL intensity from Er doped in GaAs.

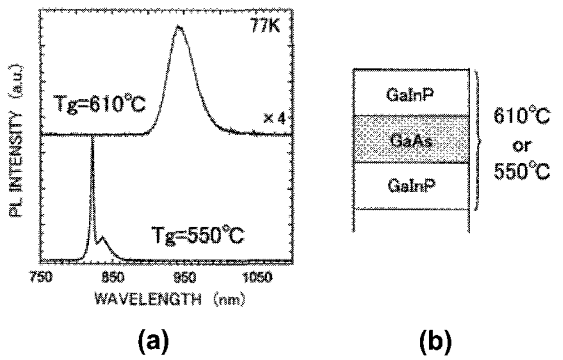

Fig. 1 (a) Photoluminescence spectra from GaInP/GaAs/GaInP structures grown at 610°C and 550°C. (b) Layer structure and growth temperatures. The three layers were grown at the same temperatures, 610°C or 550°C.

2.2 Which interface?

In Fig. 1 (b) there are two heterointerfaces, GaInP on GaAs and GaAs on GaInP. Since GaInP and GaAs are selectively etched with proper etching solutions, we removed each layer of the 580°C-grown GaAs/GaInP/GaAs structure one by one as shown in Fig. 2. Then, we measured the PL.

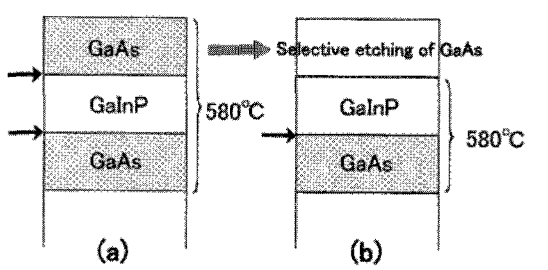

Fig. 2 (a) There are two heterostructrues in GaAs/GaInP/GaAs DH. (b) The layers were etched out selectively to find which interface is responsible for the broad emission when the structure is grown at 580°C.

It was quite easily found that the broad emission came from the GaAs/GaInP interface or from the GaAs layer very near the interface. It is because the broad emission disappeared when the top GaAs in Fig. 2 (b) was etched off, as shown in Fig. 3 (b).

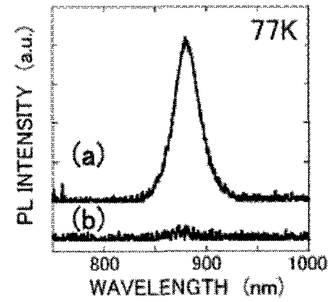

Fig. 3 The broad emission disappeared when the top GaAs was etched off. (a) is PL from the layer structure in Fig. 2 (a). (b) is PL from the layer structure after selective etching of the top GaAs.

2.3 Growth temperature effect on interfaces

The interface responsible for the broad emission was identified. Next problem to be solved is the effect of the growth temperature on the heterointerface.

The three different growth sequences were conducted. (a) The GaInP layer, interface, and the GaAs layer were all grown at 580°C. (b) The temperature was changed at the interface (GaInP was grown at 580°C. The growth temperature was lowered to 540°C before the growth of GaAs, and then GaAs was grown.) (c) The temperature was lowered during the growth of GaInP and the growth of the rest structures was continued. In the three sequences, only the sequence (c) gives a complete disappearance of the broad emission.

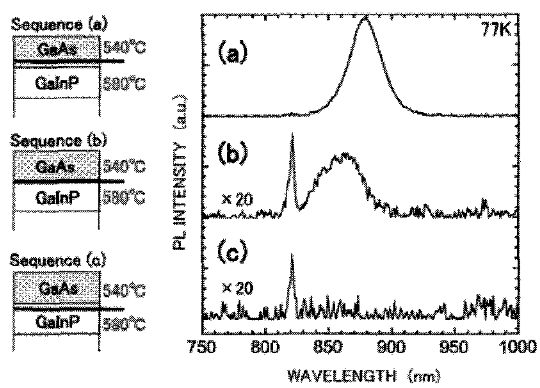

Fig. 4 In the GaAs/GaInP layer growth, the growth temperature was changed from 580°C to 540°C; (a) during the top GaAs growth, (b) just at the interface, and (c) during the GaInP growth. PL from each structure shows a clear answer that the heterointerface should be grown at a lower temperature to eliminate the broad emission.

At this stage we already suspected that In from GaInP (in gas phase or solid phase) must have distributed in the GaAs layer. However, before we conducted the X-ray CTR scattering measurements two other experiments were carried out to observe other effects of the growth temperature on layer structures and device properties.

2.4 Surface morphology

The top surface of the device structures showed a clear difference of the smoothness; smooth when GaInP and GaAs were grown at the lower temperature and less smooth when both layers were grown at the higher temperature. Each layer was selectively etched one by one to observe from which layer the smoothness changed.

The SEM observation shown in Fig. 5 gives a clear answer. The top surface of the GaInP layer grown at the higher temperature has a rough surface and its roughness is inherited to the top GaAs surface.

2.5 Device properties

With this device structure, DH lasers were fabricated and the threshold current values are plotted in Fig 6. Though the active layer was grown at 540°C in all the cases, the broad emission even at the top interface is an optical loss. The emission pass may also be a current pass that causes an increase of the threshold current. In the figure ○ is for the DH lasers of the whole layer grown at 540°C. □ and △ are for the DH lasers with the higher temperature growth process near the heterointerface. ● is for the DH lasers of the whole layer grown at 580°C. ○ occupies the lowest part in the figure and the scatter is the smallest. ● scatters largely and shows the highest values of the threshold current.

Our final target is to correlate the growth process and the device properties through the atomistic structure analysis. Up to here we understand that to obtain constant and low threshold current lasers, GaAs and GaInP interface should be grown at a lower temperature. However, we do not know what the reasons are.

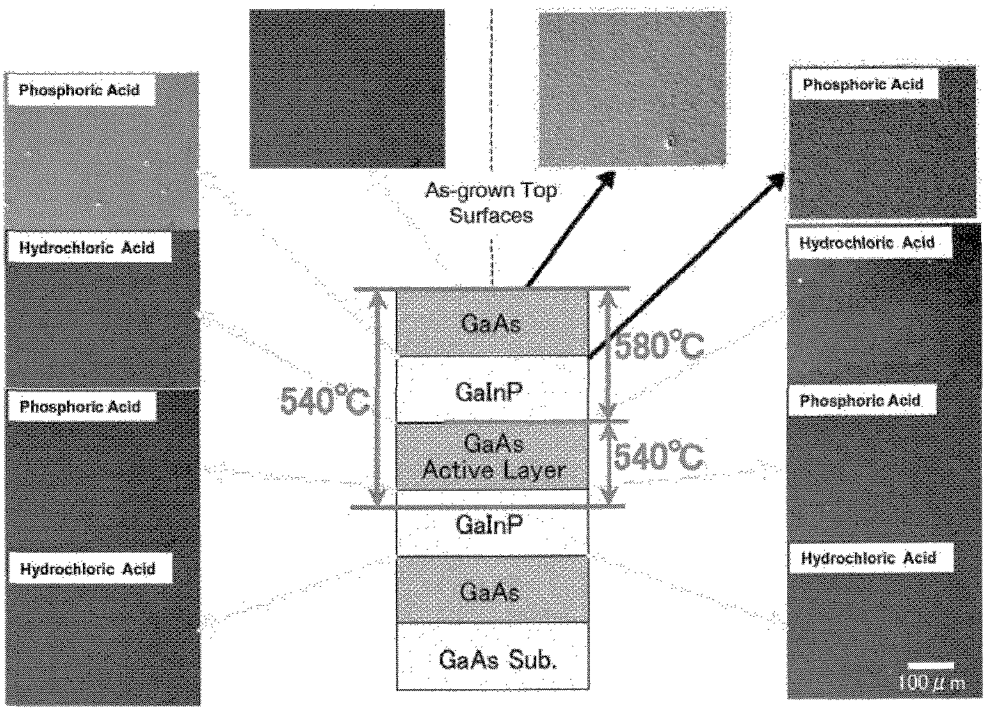

Fig. 5 SEM observation of each layer of the DH laser structure. From bottom a GaAs substrate, a GaAs buffer layer, a GaInP clad layer, a GaAs active layer, a GaInP clad layer and a GaAs cap layer for ohmic contact. The phosphoric-acid-based etching solution was used for GaAs selective etching and hydrochloric-acid-based etching solution for GaInP. The roughness starts from the GaAs/GaInP interface.

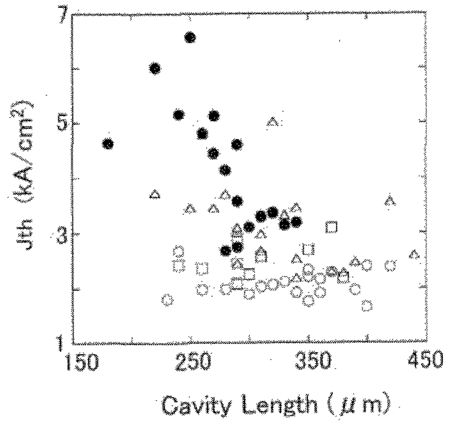

Fig. 6 Threshold currents and heterointerface growth temperatures. ○ the whole layer grown at 540°C. ● the whole layer grown at 580°C. Others contain the low temperature process. [After Ref. 26]

3. X-RAY CTR SCATTERING

What is the origin of the broad emission? What causes the roughness of the top layers? How the growth temperature affects them? Those questions still remain unsolved. The experimental evidences obtained so far strongly suggested that In from GaInP distributed in GaAs and formed GaInAs quantum well that has a lower energy gap than GaAs. Now the atomistic structure measurements are required.

3.1 Sample preparation

For simplicity of the analysis, GaAs/GaInP/GaAs structure was grown instead of GaInP/GaAs/GaInP. The thicknesses were designed as shown in Fig. 7. Fig. 8 shows where the temperatures were changed. Three samples were prepared.

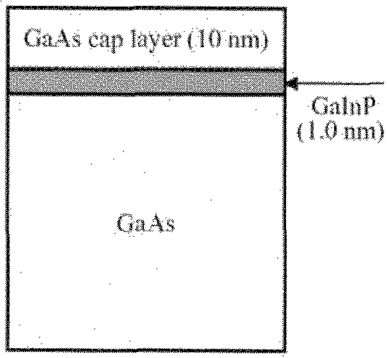

Fig. 7 Sample structure. It is simplified for the measurement convenience but contains the important heterointerface; GaAs on GaInP.

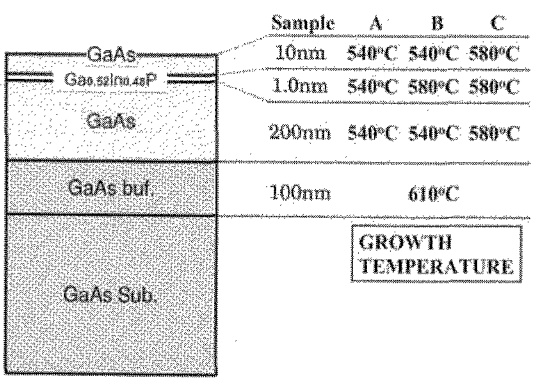

Fig. 8 Three samples with different growth sequences. Sample-A was grown at 540°C all through the layers. C was grown at 580°C all through the layers. In B the temperature was changed at the heterointerfaces.

3.2 CTR measurements and fittings

CTR measurements were conducted at the BL6A at the Photon Factory in Tsukuba. 002 Bragg point was used because its intensity is low for GaAs and higher for GaInP.

Figure 9 shows the measured CTR and fitting. The obtained In profiles are shown in Fig. 10. It is very clear that in the sample-C a considerable amount of In distributes with a long tail into GaAs to form GaInAs quantum well. We believe this well was the origin of the strong emission at 950nm. In other samples grown at the lower temperatures (whole layer or only the GaAs layer), the In distribution was much suppressed and no emission or vary weak emission was observed from samples A and B.

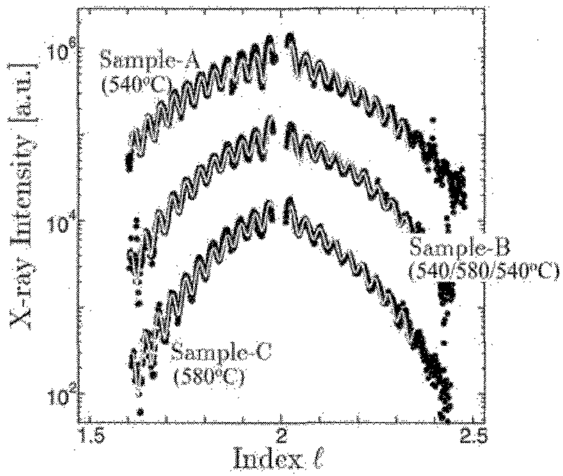

Fig. 9 Measured CTR scattering data (●) and best-fit curves (gray lines) for the three samples. 002 Bragg peaks from GaAs are truncated.

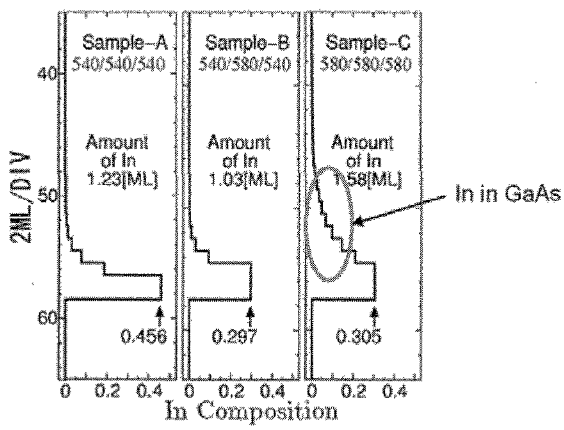

Fig. 10 Obtained In distributions in the three samples. In distribution in the sample-C is much larger and longer than those in the other samples and enough to form GaInAs quantum well in the GaAs layer that can be a recombination center for the broad emission peak. [After Ref. 26]

From the fitting shown in Fig. 9, P profiles are also obtained as shown in Fig. 11. It is clear that the P distributions are much abrupt compared with the In distribution and that in the GaInAsP transition layer near the interface effect of In is more than that of P. Thus, the energy gap of the transition layer is lower than that of either GaAs or GaInP. Abruptness of the As/P profiles was demonstrated to be easier to control [9].

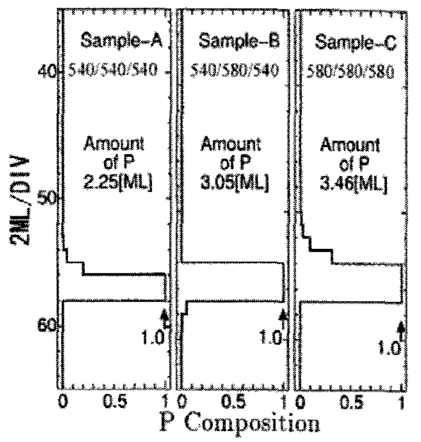

Fig. 11 Obtained P distributions in the three samples. P distributions are much abrupt compared with those of In distributions in the three samples. [After Ref. 26]

4. DISCUSSIONS

Using several experimental techniques, we can understand that the deep emission and device properties are related to the heterointerface of GaAs on GaInP. However, real answer was obtained from the atomistic measurements and analyses at the heterointerfaces. The X-ray CTR scattering technique for the buried heterostructures was the key technique.

In distribution from GaInP into GaAs as shown in Fig. 10 forms GaInAs quantum well layers, probably with different compositions and different widths, and the well layers have lower energy gaps than either GaAs or GaInP, to emit broad band near 950 nm. In the case of InP/GaInAs/InP it was shown by cross-sectional STM that the Ga and As distributions into upper InP are mainly due to a random step-wise surface (random islands in two-dimension) of GaInAs and a tail part is a diffusive distribution of As [28]. From this result we consider that the In distribution in Fig. 10 is also step-wise and it causes the non-uniform growth of GaAs on top of random islands.

The higher the growth temperature, the more the exchange between atoms at the interface should occur. It was found that the lower growth temperature suppresses the In distribution. However, the lower temperature 540°C may be too low for a device reliability. Since the suppression of In distribution was found to be essential for the high quality and abrupt interface, other techniques can be found for the suppression. For example, insertion of a very thin GaP layer on top of the GaInP before the growth of GaAs may compensate the lowering of the energy gap by containing In into GaP to form GaInP.

Thus, real understanding of the atomistic structure and its relationship to the growth process enables us to control device structures and properties.

5. SUMMARY

The X-ray reflectivity measurements around Bragg point (X-ray CTR scattering measurements) were used to reveal the buried heterostructures that are really important to understand the relationship between device structures and device properties. We started with a simple structure of As δ-doping to test the capability of the technique to reveal the structure of a buried sub-monolayer, where the crystal structure is not changed and the model is simple. It was extended to realistic structures, *i.e.*, single quantum well with different materials combinations such as InP/GaInAs/InP, InP/ErP/InP and ZnSe/GaAs.

In this paper, GaInP/GaAs/GaInP was taken as an example to show that the elucidation of the atomistic structure gives a definitive solution to the broad emission and to other phenomena including laser threshold currents. Thus, it was demonstrated that the X-ray CTR scattering measurement technique is a very powerful tool to correlate the growth process and the device properties through atomistic elucidation of the buried heterostructures nondestructively.

Acknowledgements

Due to the limited space we described only the GaInP/GaAs/GaInP heterostructures as an example. Other materials combinations were listed and described very shortly. We would like to acknowledge all the authors of those papers. The X-ray CTR measurements were performed as a part of the projects 2002G219 and 2001G239 accepted by the Photon Factory Program Advisory Committee. This work was supported in part by the Grant-in-Aid for Scientific Research (S) #18106001 from the Japan Society for the Promotion of Science.

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