Layer structure analysis of Er δ-doped InP by x-ray crystal truncation rod scattering

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(Received 26 June 1996; accepted for publication 15 April 1997)

The layer structure and crystal structure of an Er δ-doped layer in InP are analyzed in a one monolayer (ML) level by an x-ray crystal truncation rod (CTR) scattering measurement using synchrotron radiation. The Er δ-doped InP sample is prepared by organometallic vapor phase epitaxy using trimethylindium, tertiarybutylphosphine, and tris(methyl-cyclopentadienyl)erbium as source materials. The analysis is made by comparing the measured CTR spectra and theoretically generated ones assuming four possible crystal structures for the Er δ-doped layers. We reveal that the Er atoms in InP form the rocksalt structure ErP. In the analysis of the crystal structure the x-ray interference plays a vital role. Er distribution in the δ-doped layer is clearly resolved in 1 ML level. It is shown that the Er atoms are well confined in 5 ML(15 Å) thickness. The total amount of Er atoms is 0.171 ML, which is quite close to 0.2 ML obtained by Rutherford backscattering measurement on the same sample. © *1997 American Institute of Physics.*
[S0021-8979(97)05714-9]

I. INTRODUCTION

There is considerable interest in achieving good quality heterostructures of semimetallic compounds (RE-V) between rare-earth (RE) elements and group-V elements on III-V semiconductors, which may lead to new electronic devices such as resonant tunneling devices.[1] III-V compound semiconductors themselves have been applied to various electronic and optical devices using heteroepitaxial techniques. To add new functions to these III-V semiconductor devices by utilizing the semimetals of RE-V compounds, a technique to grow RE-doped layers epitaxially on III-V semiconductors and a technique to characterize the structures are necessary.

From this point of view, we have been studying δ doping of Er in InP.[2] For δ doping, both an Er doping process and a selective layer doping technique are required. At the same time, it is necessary to establish a characterization technique which can evaluate the thickness, the composition, the crystal structure, and the crystalline quality of the extremely thin layers.

The x-ray crystal truncation rod (CTR) is a rod which appears around a Bragg diffraction spot in **k** space. It is caused by the abrupt truncation of a crystal at the surface. The shape of the CTR is very sensitive to the surface roughness and difference in lattice constants.[3,4] We have demonstrated that it is a very powerful technique to reveal the layer structure of heteroepitaxially grown samples in the atomic scale.[5–8]

In this work, the x-ray scattering and interference caused by the crystal truncation and heterostructure are applied to study the Er δ-doped InP. The layer thicknesses and the distribution of Er in the δ-doped layer are clearly obtained, as is usual, by the x-ray CTR scattering analysis. In addition, it is demonstrated that the crystal structure of the δ-doped layer is determined by the x-ray CTR which is modulated by x-ray interference in heterostructures.

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II. EXPERIMENTS

A. Sample preparation

In this study, the Er δ-doped InP sample was grown by organometallic vapor phase epitaxy (OMVPE) with a vertical quartz reactor at 0.1 atm using TMIn (trimethylindium), TBP (tertiarybutylphosphine), and $Er(MeCp)_3$ (tris(methyl-cyclopentadienyl)erbium) as source materials. $Er(MeCp)_3$ was maintained at 100 °C and introduced into the reactor by a H_2 flow of 125 sccm. Details of the growth system and other growth conditions were described in Refs. 2, 9 and 10.

The time sequence of source gases to grow the Er δ-doped layer in InP is shown in Fig. 1. The growth temperature was 530 °C. An undoped InP buffer layer of 1000 Å in thickness was grown on Fe-doped InP (001) substrate. The TMIn supply was stopped to suspend the growth of InP, and the Er source was supplied for 5 min for δ doping of Er on InP. Finally a 100-Å-thick undoped InP cap layer was grown. Before and after supplying the Er source, purge periods of 30 s were inserted to ensure the source gas change. TBP was continuously supplied during these steps.

B. X-ray CTR scattering measurement

The x-ray CTR scattering measurement was conducted at the Photon Factory using synchrotron radiation from the 2.5 GeV storage ring at the National Laboratory for High Energy Physics at Tsukuba. Beam line $BL6A_2$ was used for the measurement. The wavelength of the x-ray was set at 1.600 Å by a bent Si (111) monochromator. Diffraction spots and scattering signals were recorded by a Weissenberg camera with an imaging plate (IP) as a two-dimensional detector. The signals on the IP were read out optically and

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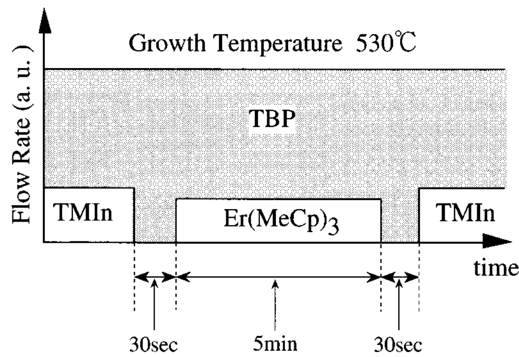

FIG. 1. Time sequence of the source gas supply for δ doping in InP with Er.

stored as digital data. The diffraction and scattering around the 002 Bragg spot were analyzed. Subtracting the background x-ray diffuse scattering from the measured x-ray intensity, we obtained the CTR spectra. In Fig. 2 an x-ray CTR spectrum with several subpeaks is shown by solid circles. The index l which appears in the figure means the index of the **k** space. In other words, we measured the x-ray CTR along the $[00l]$ direction which is normal to the surface of the sample. Subpeaks observed around the 002 Bragg point in the range from 10^4 to 10^2 are modulation caused by the existence of the Er δ-doped layer, i.e., due to the x-ray interference in the InP cap layer which is bounded by the air and the Er δ-doped layer. As will be described later, these subpeaks play a vital role in the determination of the crystal structure of the Er δ-doped layer.

III. DATA ANALYSIS

In order to analyze the data of the x-ray CTR spectrum, we made models of the layer structures and the Er atom positions in the layer, and calculated x-ray CTR scattering spectra from the models. Comparing each set of calculated spectra with the measured data, we analyzed the atom position of Er in the δ-doped layer and the Er distribution.

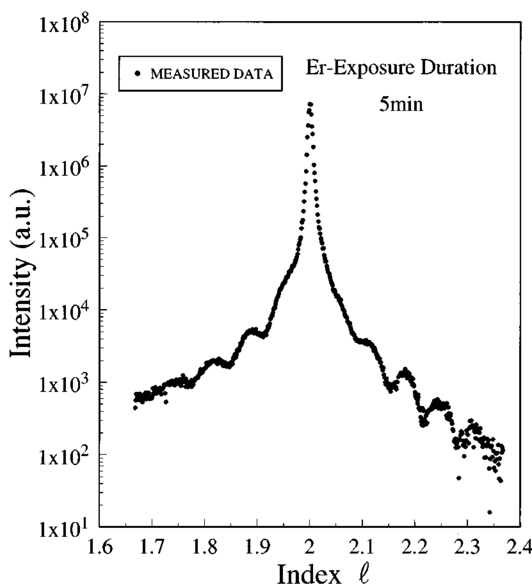

FIG. 2. Measured CTR data (●) around the 002 Bragg point. The horizontal axis is index l in $[00l]$. The InP surface was exposed to an Er source gas for 5 min for δ doping.

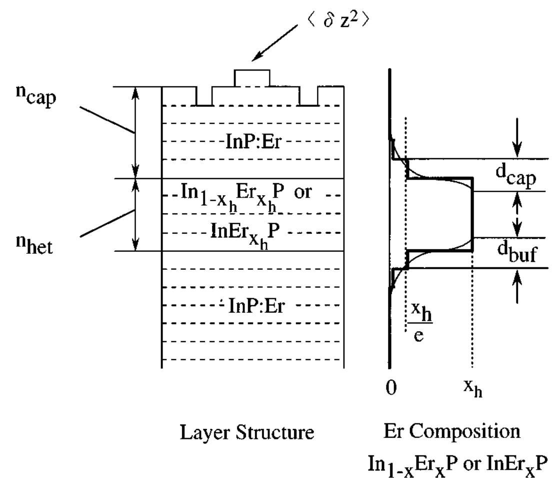

FIG. 3. Schematic drawing of the model layer structure and Er distribution.

The model of the layer structure is schematically shown in Fig. 3. This model contains seven parameters, i.e., n_{cap}, n_{het}, d_{cap}, d_{buf}, x_{h}, $\langle \delta z^2 \rangle$, and c/a. As will be described later, Er atoms were assumed to be of either substitutional or interstitial impurity in the InP matrix. When the Er atoms are included in a layer as a substitutional or interstitial impurity, the composition of the layer should be represented as $In_{1-x}Er_xP$ or $InEr_xP$, respectively. n_{cap} and n_{het} are the number of layers (in units of monolayer [ML]) of the InP cap layer and of the InErP layer, respectively. d_{cap} and d_{buf} denote the extension of the Er atoms into the InP cap layer and into the InP buffer layer, respectively. The Er distribution is assumed to have the formula

$$x = x_h \exp\{-(d/d_i)^2\},$$

where d [ML] is a distance from the upper or the lower interface. x_{h} and x are the peak Er compositions in the δ-doped layer and in the layer at the distance d [ML] from the interface, respectively. In the equation, d_i is d_{cap} or d_{buf}. $\langle \delta z^2 \rangle$ denotes the roughness of the surface. c/a indicates a tetragonal distortion of the InErP lattice, as the ratio of lattice constants normal(c) and parallel(a) to the (001) surface.

In order to investigate the Er atom position in the InErP layer, four models of crystal structure were assumed for the InErP layer. Those models are schematically shown in Fig. 4. In Fig. 4(a), Er atoms were assumed to form the rocksalt structure ErP. In Fig. 4(b), Er atoms were assumed to substitute the In site. In Figs. 4(c) and 4(d), Er atoms were assumed to be on the Td(tetrahedral) site with four P nearest neighbors and on the Td site with four In nearest neighbors, respectively. The Er composition x was varied in each monolayer in the curve fitting.

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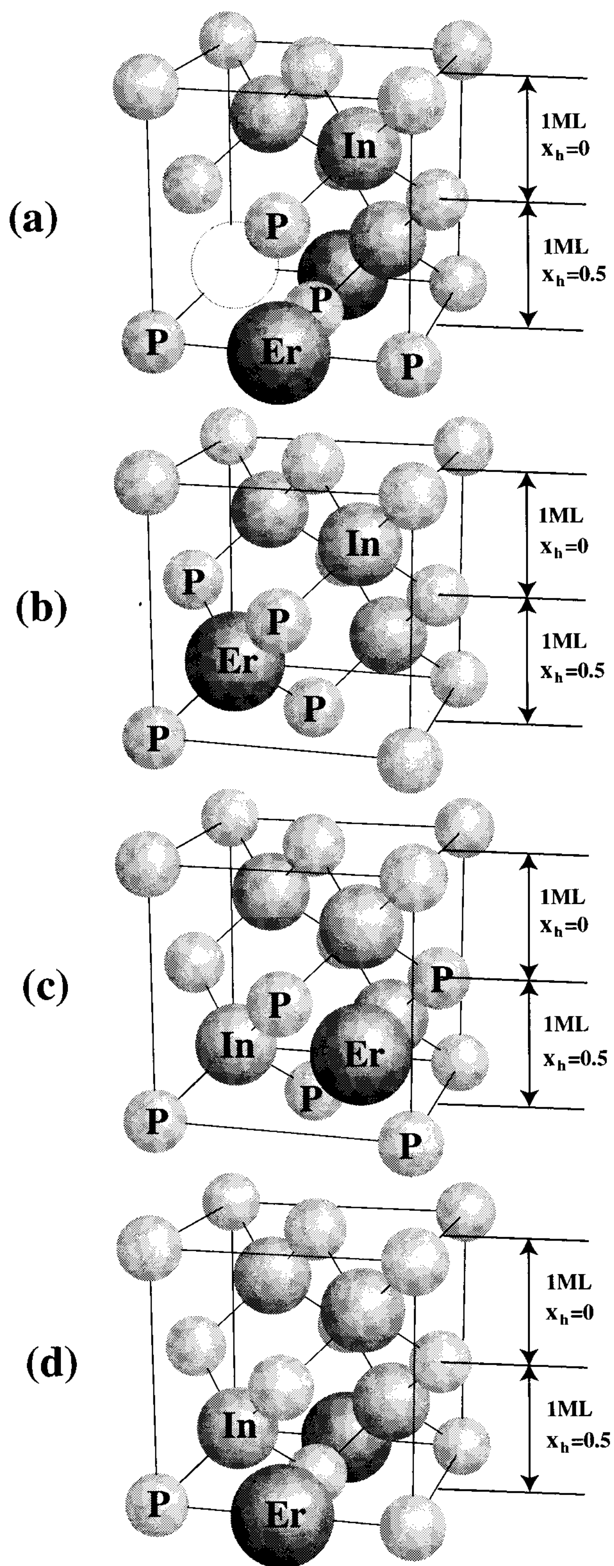

FIG. 4. Schematic drawing of model crystal structures. In (a), Er atoms were assumed to form the rocksalt structure ErP. In (b), Er atoms were assumed to substitute the In site. In (c) and (d), Er atoms were assumed to be on Td(tetrahedral) site with four P nearest neighbors and on the Td site with four In nearest neighbors, respectively.

IV. RESULTS AND DISCUSSION

In Fig. 5, the best-fit results of the four curves calculated with four different positions of Er atoms to the measured CTR spectrum around the 002 Bragg point are shown by white lines. Each pair of curves and data was shifted by two orders of magnitude to avoid overlapping. The bottom pair is shown at the intensity of the ordinate. In the process of the curve fitting, data of an index greater than 2.0 were given priority, in other words, the right-hand side of the CTR spectrum was fitted at first. Data near the Bragg peak ($1.98 < l < 2.02$) were excluded from the fitting since the intensity may be too strong for kinetic theory of the scattering, which was used for the calculation. As shown in Fig. 5, the measured CTR spectrum was fitted very well to the curve which was generated for the rocksalt structure ErP, but other curves for different crystal structures were unable to fit to the whole spectrum. It was reported that Er atoms formed the rocksalt structure of ErAs in molecular-beam-epitaxial-grown GaAs.[11,12]

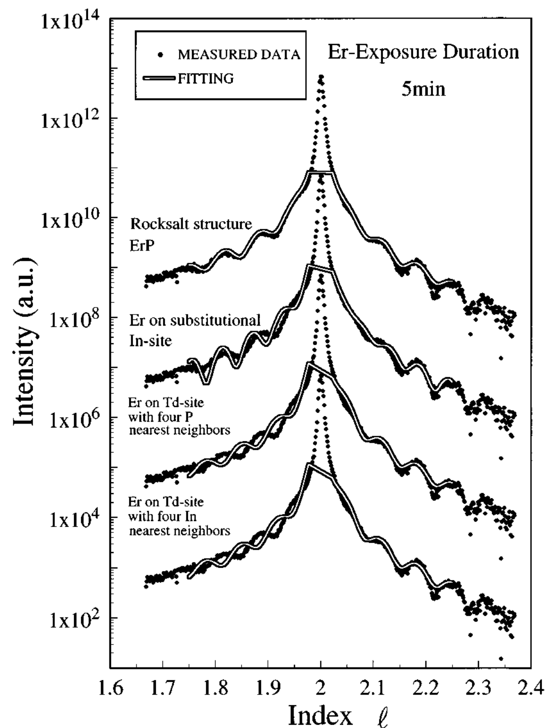

FIG. 5. The measured CTR spectrum around the 002 Bragg point is shown by solid circles. White lines are the best-fit curves calculated with each model of crystal structures in Fig. 4. Each pair of curves and data was shifted by two orders of magnitude to avoid overlapping. Data near the Bragg peak ($1.98 < l < 2.02$) were excluded from the fitting.

Values of the parameters at the best fit are listed in Table I. The thickness of the InP cap layer (n_{cap}) is nearly equal to the designed value (100 Å). When the thickness of the InErP layer n_{het} which is shown in Fig. 6 as the full width at half-maximum (FWHM) is taken into the cap layer thickness, ($n_{cap} + n_{het}$) is quite close to 100 Å. The value of $\langle \delta z^2 \rangle$ was

TABLE I. Values of fitting parameters at the best fit to the measured data. Er atoms form the rocksalt structure ErP in the δ-doped layer.

n_{cap}	$\langle \delta z^2 \rangle$	c/a	Total Er atoms
30 ML(88 Å)	0.104 ML^2	0.983	0.171 ML

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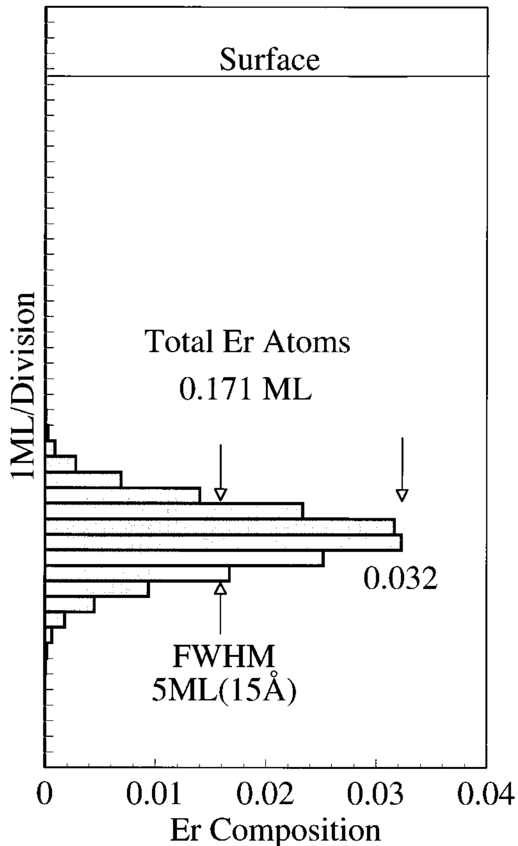

FIG. 6. Obtained Er distribution. The peak Er composition is 0.032 and the full width at half maximum (FWHM) is 5 ML(15 Å). The amount of Er is calculated as the area of dark region. It is 0.171 ML.

0.104 ML^2. It means that the top surface of the InP cap layer was quite flat. The value of c/a was 0.983, which is close to the calculated value of 0.985 with the lattice parameters of InP (5.8694 Å) and ErP (5.606 Å), respectively, and the assumed Poisson's ratio of ErP (1/3, to our knowledge, there is no data of it).[13]

The obtained distribution of the Er atoms is shown in Fig. 6 on the monolayer scale. The FWHM of the Er distribution was 5 ML (15 Å). The Er distribution profile is almost symmetric. The Er peak composition was 0.032 and the total amount of Er atoms was 0.171 ML. This amount is quite close to 0.2 ML, which was obtained from the Rutherford backscattering measurement on the same sample.[9]

All the results shown above indicate that the x-ray CTR measurement with interference can reveal the distribution of the Er atoms with the resolution of an atomic scale and even the crystal structure in the layer.

V. CONCLUSION

The sample of Er δ-doped InP was prepared by OMVPE. The δ-doped layer was formed by exposing the InP surface to an Er source gas for 5 min at 530 °C. The layer structure of the Er δ-doped InP was analyzed by the x-ray CTR scattering measurement and x-ray interference using synchrotron radiation. From the result of the measurement and computer simulation, we revealed that the Er atoms δ doped in InP formed the rocksalt structure ErP. The Er distribution was resolved on the order of one monolayer (ML). Er atoms in the Er δ-doped InP layer were found to be confined in 5 ML(15 Å).

ACKNOWLEDGMENTS

This work was performed as a part of the project (Project No. 94G331) accepted by the Photon Factory Program Advisory Committee. This work was supported in part by the Grant-in-Aid for Developmental Scientific Research (B) No. 07555100 from the Ministry of Education, Science and Culture.

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