Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984, pp. 201-204

Compositional Inhomogeneity of InGaAsP/GaAs LPE Layer by Precision X-Ray Diffractometry

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The effects of growth conditions on compositional inhomogeneity of InGaAsP LPE layers on (100)GaAs were studied by precision X-ray diffractometry. The compositional fluctuation, taking place at initial growth stage (less than several seconds) during growth, is attributed to the initial supersaturation ΔT rather than the lattice mismatch, the temperature fluctuation, or the phosphorus adhesion to GaAs. Using the In-Ga-P phase diagram, it was found that ΔT affects the crystallization path esp. at initial growth stage. In order to minimize the compositional inhomogeneity ΔT should be as small as possible.

1. Introduction

The quaternary III-V compound InGaAsP grown on GaAs has received much attention as a material for visible-light emitting devices. In the device application of the heterostructure, one of the most important properties is the compositional uniformity. A double crystal X-ray diffractometry makes it possible to study the solid composition precisely by measuring the lattice constant. In addition, the lattice mismatch in the direction perpendicular as well as parallel to the hetero-interface can be estimated from asymmetric reflections of X-ray.

Several authors studied the compositional inhomogeneity of InGaAsP on InP using the double crystal X-ray diffractometry, and reported a compositional variation,[1-3] which was characteristic at short time growth (less than several seconds).[3] This variation was supposed to be attributed to non-diffusion-limited process such as a convection current due to a motion of a substrate or attachment kinetics of solute atoms.[3,4] But the details are not well known, and it is desirable to study the effects of the growth conditions especially at short time growth on compositional nonuniformity.

In this work the compositional inhomogeneity in InGaAsPn(100)GaAs LPE layers are measured using the high resolusion double crystal X-ray diffractometry by (511) asymmetric reflection, and the compositional variations are investigated in relation to the various growth conditions: the lattice mismatch, the initial supersaturation, the temperature flactuation, and phosphorus adhesion to GaAs. The lattice deformation of the layers due to the lattice mismatch is also shown.

2 Experiment

Epitaxial layers of $In_xGa_{1-x}As_yP_{1-y}$ ($y<0.01$) were grown on (100)GaAs using a horizontal sliding boat and ramp-cooling (supercooling) technique.[5] Solute concentrations in In melt were chosen to prepare a quaternary layer with band gap of about 1.9eV(λ_p=6500Å); $X_{Ga}{}^1$=0.86-1.04at%, $X_{As}{}^1$=0.03at% and $X_P{}^1$=2.80at%. After the melt was kept at 800°C, it was cooled at a rate of 0.5°C/min and touched with the substrate at 776-786 °C (T_g). The initial supersaturation was determined as a difference in T_g and T_s (equilibrium saturation temperature). The latter was estimated experimentally.[5] The layer thicknesses obtained were 1-2μm.

X-ray double crystal rocking curves (XRC's) were measured for two arrangements (A and B settings) in (511) asymmetric reflection of CuKα_1 radiation as well as (400) symmetric one.[6] The

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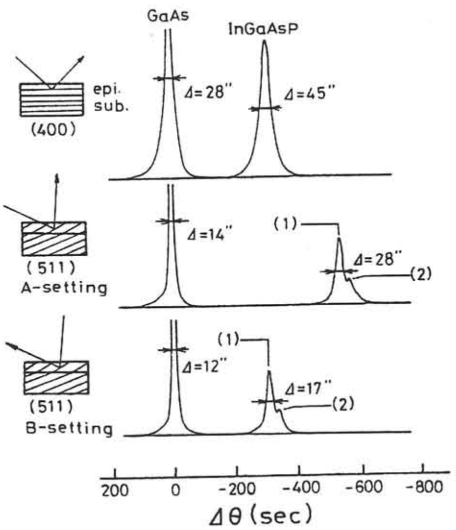

Fig.1 X-ray rocking curves for the (400), (511)A and (511)B setting reflections.

typical examples of the XRC's are shown in Fig.1. The half widths of the (511)A and (511)B peaks are about a half of (400) one. Furthermore, the XRC's for the layer in the (511) reflections exhibit two peaks ((1) and (2)), suggesting that there is a compositional inhomogeneity in the epitaxial layer. In this work the (511) reflections are studied in detail.

3. Results

(3.1) Effects of lattice mismatch

In order to study the effects of the lattice mismatch, $X_{Ga}^{\,l}$ was varied from 0.86 to 1.04at%, where ΔT was 3.0°C and t_g was 2 min. Smooth mirror-like surfaces were obtained under these conditions. Figure 2 shows the XRC's of (511)A reflection for various $X_{Ga}^{\,l}$. All XRC's of the layers are composed of two peaks ((1) and (2)) and the difference in between is almost independent of $X_{Ga}^{\,l}$. To investigate the origin of this compositional inhomogeneity, the (511)A XRC's were measured successively by repeating step-etching of the epilayer. The results are shown in Fig.3, which shows that the lattice constant varies stepwise during growth from the peak (1) to (2) along the thickness. The growth time to form the initial layer for the peak (1) is estimated at about 5sec from the growth rate.[5)]

The lattice deformation of the layer due to the lattice mismatch was calculated from the XRC's of the (511)A and (511)B settings.[1,6)] This results (Fig.4) show that epilayers are tetragonally deformed, i.e., the normal lattice mismatch $|(\Delta a/a)_\perp|$ is as large as $4\mathrm{x}10^{-3}$ while the lateral one $|(\Delta a/a)_\parallel|$ is less than $1\mathrm{x}10^{-4}$ for both peaks. It is also shown that the compositional variation from the peak (1) to (2) is independent of the lattice mismatch.

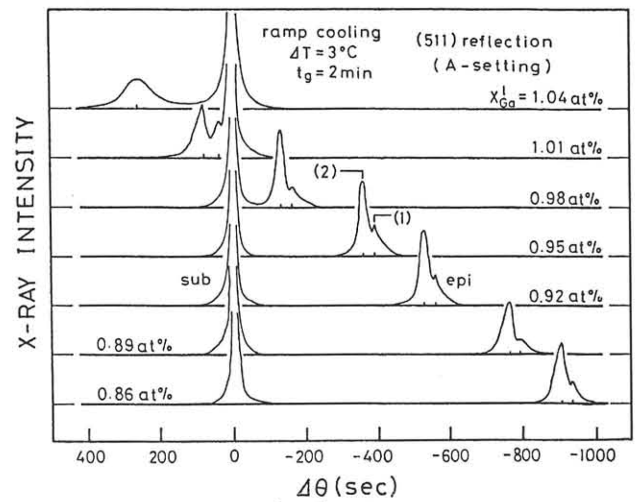

Fig.2 X-ray rocking curves using the (511)A asymmetric reflection for InGaAsP (about 1.3μm thick) grown on (100)GaAs for the various solute concentratins of $X_{Ga}^{\,l}$=0.86-1.04at%.

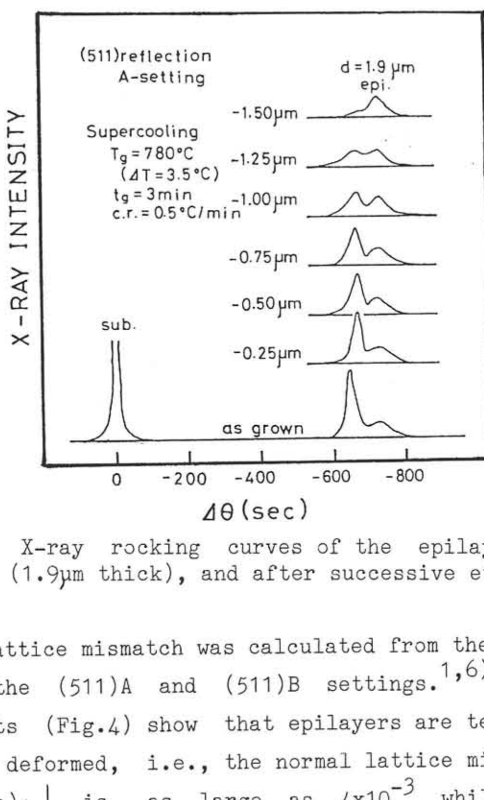

Fig.3 X-ray rocking curves of the epilayer as-grown (1.9μm thick), and after successive etching.

(3.2) Effects of initial supersaturation

The initial supersaturation was varied; ΔT=0-10 °C, while the solute concentrations were fixed at $X_{Ga}^{\,l}$= 0.95at%, $X_{As}^{\,l}$=0.03at% and

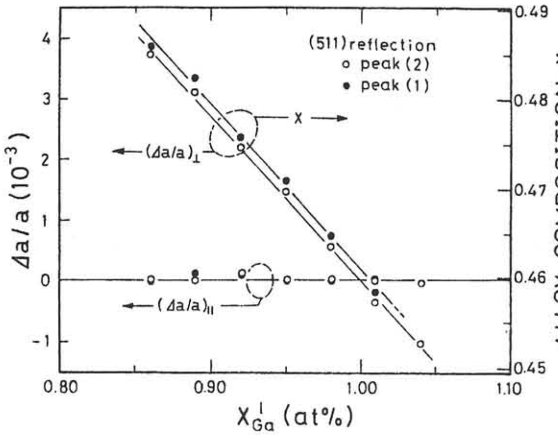

Fig.4 Lattice mismathes and alloy composition as a function of X_{Ga}^{l} for the peaks (1) and (2). $(\Delta a/a)_\perp$ and $(\Delta a/a)_\parallel$ show the lattice mismatches normal and parallel to the substrate surface, respectively.

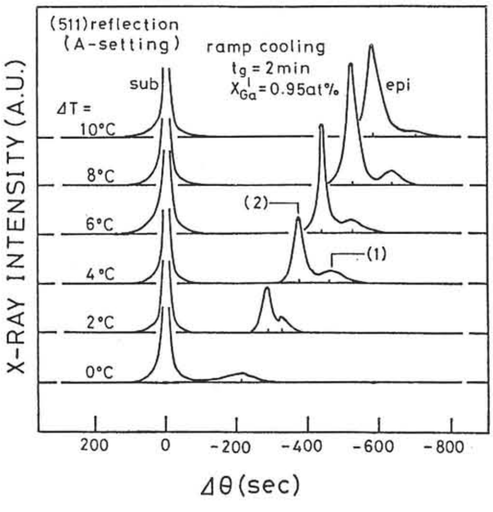

Fig.5 X-ray rocking curves of the epilayers (1-2μm thick) grown for the various initial supersaturations of ΔT=0-10 °C.

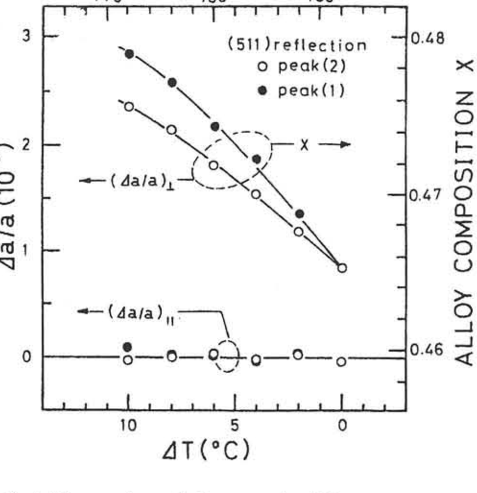

Fig.6 Lattice mismatches and alloy composition as a function of ΔT for the peaks (1) and (2).

X_P^l =2.80at% so that the equilibrium saturation temperature T_s was 786 °C. The growth time was 2min and the layer thickness was 2μm. As seen in Fig.5, all XRC's of the layers are also resolved into two peaks ((1) and (2)) except ΔT=0 °C. Fig.6 shows the normal and lateral mismatches and its solid composition x for the peaks (1) and (2) as a function of ΔT. The difference between the peaks (1) and (2) increases by increasing ΔT.

It is therefore concluded that the compositional inhomogeneity at the initial stage of the growth strongly depends on ΔT. Hence, in order to minimize compositional inhomogeneity, the initial supersaturation should be as small as possible.

(3.3) Other effects

The effects of the temperature shift during the growth were studied by measuring the XRC's of the layers grown by the step-cooling technique for comparison. It was found that these XRC's had two peaks and agreed well with those for the ramp-cooling one. This suggests that the stepwise variation is not caused by the temperature variation.

The phosphorus molecules vaporized from the source melt might adhere to the GaAs substrate before growth.[7,8] This might change the solid composition at the initial stage of the growth. We compared the XRC's of the layers grown on the substrate with and without the etching process using under-saturated Ga melt of As solute before growth, where the etched layer thickness was about 1μm. The XRC's for the both cases agreed with each other. Hence, the effect of the adhesion of P atoms can be neglected.

4. Discussion and Conclusion

It has been shown that the compositional variation at the initial stage depends on ΔT, which affects the solute concentration profiles near the interface especially at the initial stage and fluctuates the crystallization path in the phase diagram. Then we discuss such compositional variation using the crystalization path in the In-Ga-P phase diagram.

The phase diagram was calculated on the basis of the regular solution model of Illegems and Panish.[9] Well-accepted thermodynamic parameters were used in the calculation.[10] The effect of the lattice mismatch strain in the epilayer was considered as a sum of the mismatch strain energy.[11] Figure 7 shows the calculated results for the liquidus and solidus lines together with the experimental data for various ΔT (0-10°C), where the solute concentrations of Ga and P were fixed at 0.95 and 2.80at%, respectively. The crystallization pathes from the peak (1) to (2) in the XRC's exist along the liquidus isotherms because such variations take place for short time. Fig.7 shows that the solid composition is determined on the line A for initial short period (t_g<10sec) and then shifts into the line B.

The compositional variation is attributed to the change of the solute concentration profiles near the growth interface at initial growth stage.[12] Since the gradients of the solute concentrations at the interface are large at the initial stage, the difference in the diffusion velocities of the solutes (P and Ga) can be so large as to cause the change in the quantites of the solutes reaching to the growth interface and hence the compositional variation in solid. If the diffusion coefficient of Ga (D_{Ga}) is smaller than that of P (D_P), relatively small Ga solid fraction (1-X) is obtained along the line A. On the other hand, the gradients of the concentrations decreases by increasing the growth time. Since the difference in D_{Ga} and D_P is not significant to determine x, the crystallization path can move into the line B. Hence, it is concluded that the larger compositional variation is caused by the larger supersaturation.

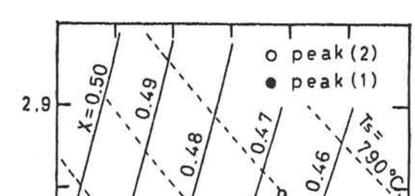

Fig.7 Crystallization pathes from the peak (1) to (2) for the different initial supersaturations of ΔT=0-10°C in the In-Ga-P phase diagram which includes liquidus and solidus curves. The solute concentrations of Ga and P were fixed at 0.95 and 2.80at%, respectively.

In conclusion, the effects of the growth conditions on the compositional inhomogeneity of InGaAsP/(100)GaAs were studied by the precision X-ray measurement. It was found that the compositional fluctuation at intial growth stage is due to the initial supersaturation, which changes the crystallization path in the phase diagram.

Acknowlegements

The authors wish to thank Dr. Y.Toyoda with Matsushita Electric Ind. Co. for his help in carrying out the measurements of the double crystal X-ray diffractometry and for valuable discussions. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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