A Study of Heteroepitaxy of InP on GaAs by Metalorganic Vapor-Phase Epitaxy

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ABSTRACT

The epitaxial layers of InP were grown on a GaAs substrate by atmospheric pressure metalorganic vapor-phase epitaxy. By employing a two-step growth procedure, an epitaxial layer with a specular surface and good crystalline quality could be obtained when a thin buffer layer (~ 200Å) was deposited at low temperature (400°C) prior to the epitaxial growth. On the other hand, in the case of direct growth, a growth layer had a rough surface and poor crystalline quality, presumably due to island-like growth and/or reaction of PH_3 gas with GaAs in the early stage of epitaxy. Compressive stress and strain in the epitaxial layer was measured from the shift of the photoluminescence peak energy between the hetero- and homoepitaxial layers. The strain and stress was 1×10^{-3} and $\sim 1 \times 10^{-9}$ dyn/cm^2, respectively, which was explained by the difference of the thermal expansion coefficient between InP and GaAs.

Highly lattice-mismatched heteroepitaxy such as GaAs on Si has attracted a great deal of attention for preparing an optoelectric integrated circuit (OEIC) and low-cost solar cells with high efficiency (1, 2). InP and InGaAsP on GaAs would be another candidate for OEIC's with higher performance. For example, InGaAsP/InP/GaAs heterostructure could be used as lasers or detectors with low-loss wavelength (~1.6 μm) for optical fibers, as well as GaAs ICs with higher processing ability than Si ICs (3). Moreover, coupling with an optical fiber in an InGaAsP/InP/GaAs optical device would be simplified since the laser beam emitted from the InGaAsP active layer can penetrate both InP and GaAs. To achieve such a heterostructure, high-quality InP epitaxial growth on GaAs is the key technology, since lattice-matched InGaAsP layers on InP could be easily performed (4). There is relatively large lattice mismatch (~3.8%) for InP/GaAs heterostructure which is almost the same as that for GaAs/Si. On the other hand, the difference of thermal expansion coefficient between InP and GaAs is relatively small ($1.5 \times 10^{-6}K^{-1}$) compared with that of GaAs/Si ($2.7 \times 10^{-6}K^{-1}$). Therefore, lower thermal stress in InP epitaxial layer would be expected during the growth process. However, very little attention has been paid to the study of heteroepitaxy of InP on GaAs (3, 5, 6).

In this paper, crystalline and surface morphological natures of InP epitaxial layers on GaAs grown by metalorganic vapor-phase epitaxy (MOVPE) both with direct and two-step growth procedure were investigated.

Experimental

A standard MOVPE growth system was employed in this experiment and operated under atmospheric pressure. Trimethylindium (TMI) and 10% phosphine (PH_3) in hydrogen (supplied from Morton Thiokol, Incorporated, Alfa Products, and Nippon Sanso Company, Limited, respectively) were used as source materials. TMI was maintained at 17°C and introduced into the reactor with pure N_2 gas. Pd-diffused H_2 was used as the carrier gas. For 2 min, (100) GaAs substrates were etched in the hot H_2SO_4-H_2O_2-H_2O (4-1-1 at 50°C) solution.

Two kinds of growth processes were tried, direct and two-step growth, to find the optimum growth condition. The growth parameters are summarized in Table I where the high [Ph_3]/[TMI] molar ratio of ~500 was employed for the growth of buffer layers to decompose PH_3 at the low temperature of ~400°C (7). The surface morphologies of InP epitaxial layers were observed with a conventional Nomarski interference optical microscope and a scanning electron microscope (SEM). Also, Auger electron spectroscopy (AES) was used to study an initial growth mechanism. Crystalline quality of epitaxial layers was measured by the x-ray rocking curves (ω mode) and the diffraction profiles (2θ/θ mode) with double crystal Si(200)-InP/GaAs (400) using CuKα_1. A lattice spacing distribution associated with the fluctuation of the lattice constant was measured from a diffraction profile, and an orientation distribution related with misorientation was determined from the rocking curve by ω mode with a narrow detector slit admitting x-rays diffracted from a given spacing to pass through exclusively (a technique newly developed by N. Ito (8). Photoluminescence measurement from near the emission edge was performed to estimate the residual stress in the InP epilayers with an excitation source of Ar^+ laser (488 nm).

Results and Discussions

Figure 1 shows typical surface morphologies of as-grown InP epitaxial layers on GaAs substrates both for direct and two-step growth procedures in the growth temperature range of 550°-650°C. For all samples, the thickness of the epitaxial layers was about the same (~1.2 μm). In the case of two-step growth, a specular surface was obtained at the growth temperature of 650°C. However, in the case of direct growth, only a rough surface could be obtained. To clear the difference of surface morphologies between direct and two-step growth, the early stage of epitaxial growth was investigated. Figure 2 shows surface microphotographs taken by SEM for thin epitaxial layers (~1000Å). For low-growth temperatures (<550°C), a smooth surface could be obtained as shown in Fig. 2(a). However, island-like growth occurred at the high-growth temperatures (>600°C). For the island-like surface, AES spectra were measured both on a plateau of an island and a flat region (as shown in Fig. 3) where an electron beam probe was focused in AES within several thousand Angstroms. From the spectrum at the plateau region, In and P peaks could be observed (denoted B in Fig. 3). On the other hand, at the flat region Ga and As peaks appeared in addition to In and P peaks, presumably from the signal of the GaAs substrate. The escape depth of AES electron is seen to be very small (less than a few tenths of Å) (9). Therefore, the island-like growth might be explained by the Stransky-Krastanov mechanism (10).

The comparison of a crystalline quality between direct and two-step growth was performed by a measurement of

Table I. Growth parameters for InP/GaAs MOVPE

	Two-step growth		
	Predeposition	Epitaxial growth	Direct growth
Growth temperature (°C)	400	550-700	550-700
$[PH_3]/[TMI]$ molar ratio	504	38	38
TMI flow rate (cm^3/min)	50	200	200
Growth rate (μm/h)	~0.5	~2.4	~2.4
Growth time (min)	0.5-8	30	30

Table II. Orientation distribution terms ($\Delta\theta_1$) and lattice spacing distribution terms ($\Delta\theta_2$)

Growth method	Growth temp. (°C)	Thickness of buffer layer (Å)	FWHM of x-ray ω mode (min)	$\Delta\theta_1$ (min)	$\Delta\theta_2$ (min)
Direct	550	0	9.2	—	—
	650	0	17.2	14.0	1.5
Two-step	550	200	9.8	7.8	1.5
	600	200	8.8	6.6	1.5
	650	200	7.8	5.8	1.1
	700	200	9.0	7.0	1.2

$2\Delta\theta_2$ corresponds to the value ordinary performed by x-ray diffraction profile with θ- 2θ scan. FWHM of x-ray ω mode is approximately expressed as $\Delta\theta_1 + \Delta\theta_2$ (8).

x-ray rocking curves. Figure 4 shows the full width at half maximum (FWHM) dependence of the rocking curves for various growth temperatures. For the two-step growth, the FWHM was found to be minimum at the growth temperature of 650°C. In the case of direct growth, the FWHM increased considerably as the growth temperature was increased. The FWHM was separated into an orientation distribution term ($\Delta\theta_1$) and a lattice spacing distribution term ($\Delta\theta_2$) (as denoted in Table II) where 2 $\Delta\theta_2$ gives a FWHM in the diffraction profiles for the θ-2θ scan (8). These values were with errors less than 6s of arc. From this result, these temperature dependences may be considered mainly due to the orientation distribution in the InP epitaxial layers, because the spacing distribution is rather small for all samples. Therefore, InP layers might have a kind of mosaic structure, presumably very near the interface, *i.e.*, the lattice plane of InP would be inclined and fluctuate microscopically against the lattice plane of the GaAs substrate.

Considerations as to the origin of the large orientation distribution for direct growth follows. In one origin of the orientation fluctuation, it might be considered that the growth was performed by the coalescence of islands, each

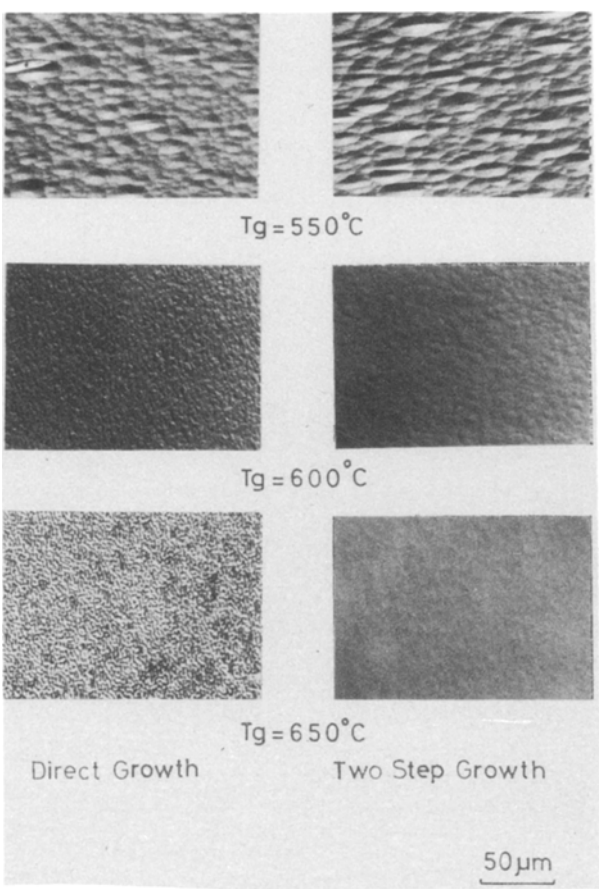

Fig. 1. Surface morphologies of InP on (100) GaAs substrate for the direct and the two-step growth in the growth temperature range of 550°-650°C.

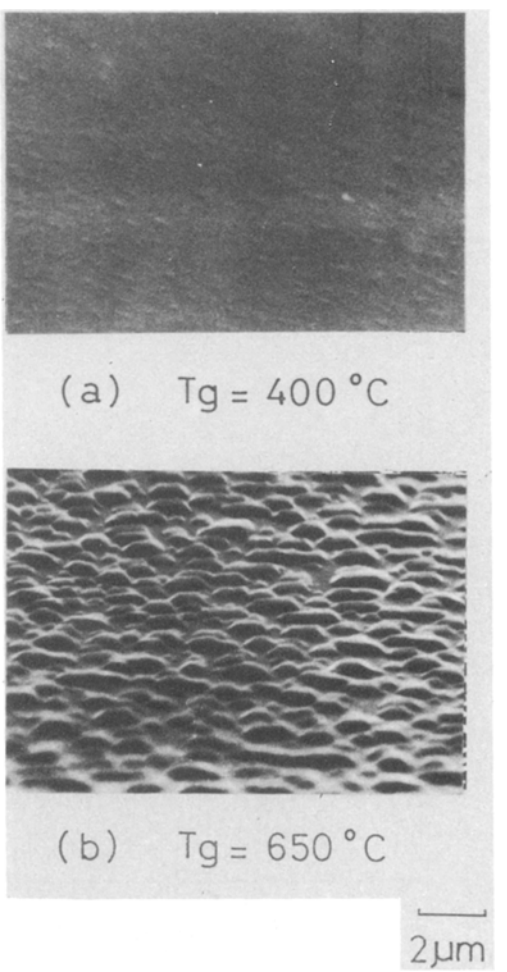

Fig. 2. SEM images for early stage of heteroepitaxial-grown surfaces for a lower and a higher growth temperature. Average thickness was ~0.1 μm for both cases.

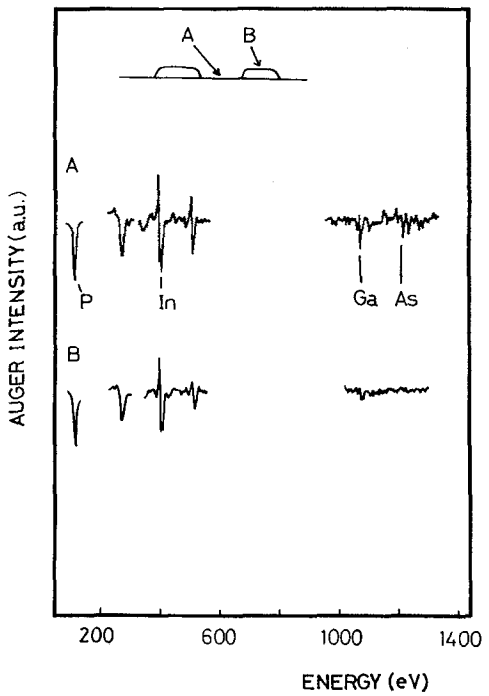

Fig. 3. AES profiles taken at the flat region (denoted as A) and the plateau region of an island (denoted B) for the sample grown at 650°C with the average thickness of ~0.1 μm. The same sample shown in Fig. 2(b) was used.

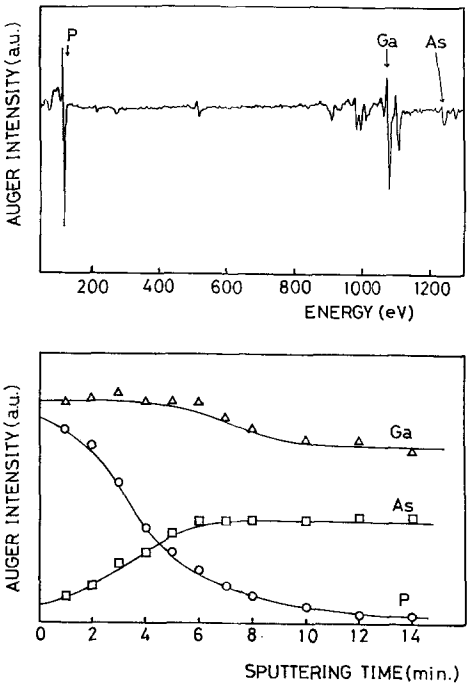

Fig. 5. AES depth profile graph for the annealed sample of (100) GaAs at 650°C for 5 min under PH_3 atmosphere with partial pressure of 7×10^{-3} atm and the as-treated AES profile (upper graph). Sputtering rate of GaAs was 15 Å/min.

island having a different orientation. As to the other origin, it might be thought that all islands have a same orientation and the lattices around the island boundaries are deformed having the other orientation when the islands grow and coalescence occurs. A further study of which origin is dominant in the present case is now underway and will be presented elsewhere.

Another important factor influencing the orientation dependence might be the thermal reaction of phosphorus with a GaAs substrate previously observed by Hsu *et al.* (11) and Mukai *et al.* (12). The reaction was investigated by annealing the GaAs substrate in PH_3 atmosphere in the temperature range of 550°-650°C. From the AES depth profile, a GaAsP layer was formed due to the reaction with PH_3 and a GaAs substrate. The reaction was excessive above the temperature of 600°C (see Fig. 5). This GaAsP layer may cause an inhomogeneous lattice deformation of the substrate surface which may result in enhancement of the orientation dependence. However, in the two-step growth, the reaction will be small resulting in the rather small FWHM and orientation dependence.

In the case of the two-step growth, the x-ray FWHM depended on the thickness of the buffer layer. The minimum value of FWHM was obtained at the buffer layer thickness of 200Å as shown in Fig. 6. In the case of thinner buffer layers (<200Å), the predeposited layer might become very small islands when the substrate temperature was raised to the elevated substrate temperature and the coalescence

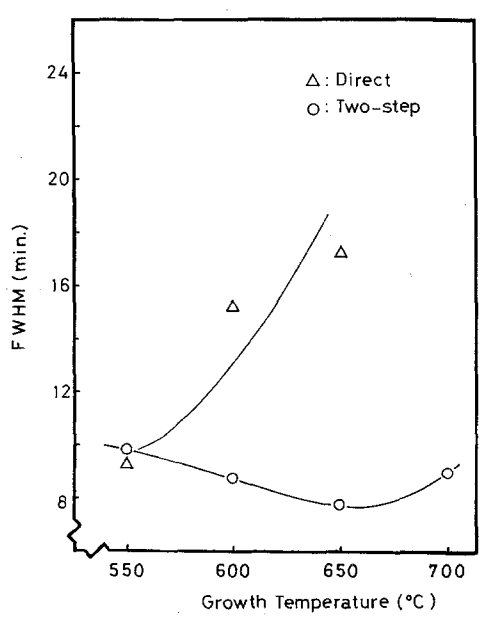

Fig. 4. A full width at half maximum of x-ray rocking curves *vs.* growth temperature for the direct and the two-step growth process. Data was taken for the samples with the same epitaxial layer thickness (~1.2 μm).

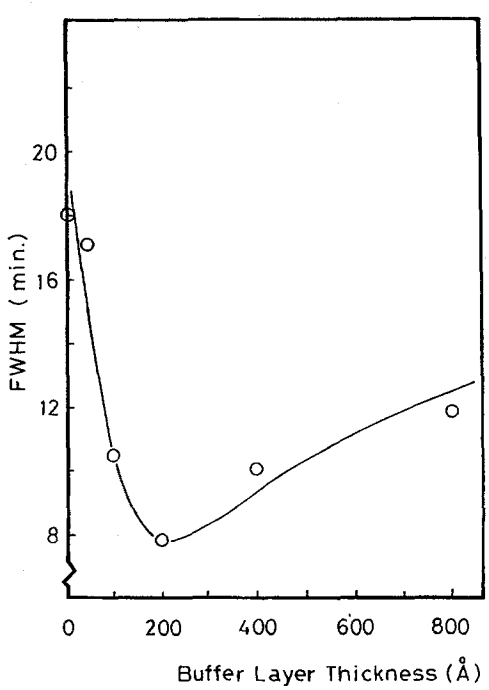

Fig. 6. A change of x-ray FWHM associated with the buffer layer thickness at the two-step growth procedure. The predeposition and the epitaxial growth temperature was kept constant to 400° and 650°C, respectively. The total thickness was the same (~1.2 μm).

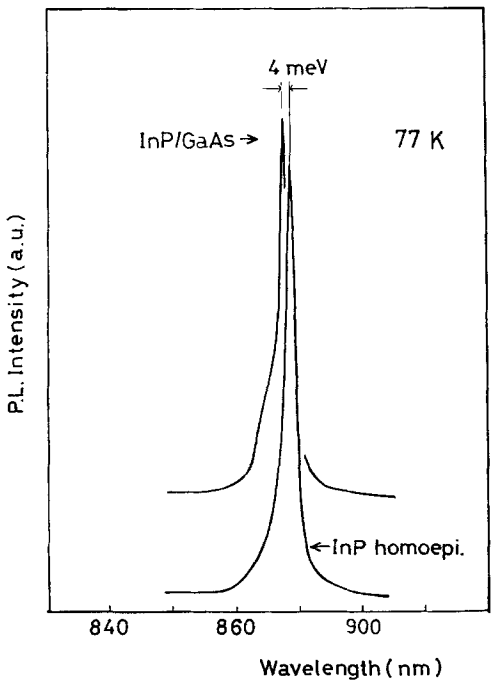

Fig. 7. PL spectra (77K) both of a two-step grown InP/GaAs and an InP homoepitaxial layer. These samples were with the same electron carrier concentration of 1×10^{16}cm^{-3}.

of these islands would result in the deterioration of the crystalline quality. For the thicker buffer layers (>200Å), some kind of spontaneous nucleation in the buffer layer might occur as the substrate temperature is increased as suggested by Akiyama *et al.* (13).

The strain of an InP epitaxial layer grown by the two-step growth was estimated from the peak energy shift (ΔE) of the photoluminescence (PL) spectra. Related to the strain, ΔE can be expressed as follows (14)

$$E = \left\{ \frac{2a(C_{11} - C_{12})}{C_{11}} + \frac{b(C_{11} + 2C_{12})}{C_{11}} \right\} \epsilon \qquad [1]$$

where C_{ij} is the elastic stiffness, a the hydrostatic deformation potential, b the shear deformation potential, and ϵ the strain. As shown in Fig. 7, ΔE was ~4 meV for the sample at the growth temperature of 650°C.

The PL intensity and the half-width was comparable with the InP homoepitaxial layers. By using Eq. [1] and InP data (14), the compressive strain was $\sim 1 \times 10^{-3}$ which corresponded to a compressive stress of $\sim 1 \times 10^{9}$ dyn/cm^2. The stress and strain is much lower than the value reported for GaAs/Si (15). Also, these values could be explained approximately due to the difference of the thermal expansion coefficient between InP and GaAs. Therefore, the InP/GaAs heterostructure would be attractive both for OEICs and low-cost InP substrates.

Conclusions

The heteroepitaxy of InP on GaAs was studied by metal-organic vapor-phase epitaxy. The two-step growth procedure was effective to improve the surface morphology and the crystalline quality of epitaxial layers. In the case of direct-growth procedure, an island-like growth was dominant above the growth temperature of 600°C. The stress in an InP heteroepitaxial layer was compressive which was corresponded to the difference of the thermal expansion coefficient between InP and GaAs.

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A Study on HCl Intrinsic Gettering for Application to Bipolar Devices and MOS LSI's

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ABSTRACT

The three-step preheat-treatment using HCl oxidation has been investigated in order to develop an effective and sure gettering technique. In this technique the bulk oxidation-induced stacking faults play a role of gettering sinks. The junction leakage failure of high-speed bipolar devices was suppressed by this HCl intrinsic gettering through complete elimination of epitaxial stacking faults. Furthermore, the HCl intrinsic gettering was applied to a MOS image sensor and a dynamic RAM to improve their yield performance.

Process-induced defects adversely affect circuit performance and yield of both high-speed bipolar and MOS LSIs (1, 2). The effects on yield are more detrimental with higher levels of integration. Furthermore, circuit failure of high-speed bipolar devices is very sensitive to process-induced defects because of shallow junctions (3). Elimination of these defects is a critical issue in both bipolar and MOS LSIs. A large number of gettering techniques have