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# Replacement of Surface In Atoms by Ga during Migration-Enhanced Epitaxy

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An InAs monolayer is grown between GaAs layers by migration-enhanced epitaxy. Reflection high energy electron diffraction observation during the growth and secondary-ion mass spectroscopic analysis of the grown layers show that some surface In atoms in the InAs monolayer are replaced by subsequently deposited Ga atoms. Atomic layer superlattice structure is self-organized by growing an InGaAs layers on an InP substrate with the deposition of two monolayers of mixed metallic atoms per cycle in migration-enhanced epitaxy. A similar superlattice structure is organized also in a GaAs/AlAs system.

## 1. Introduction

Recently, many kinds of optical and electrical devices have been fabricated using heteroepitaxy of compound semiconductors, such as AlAs/GaAs or InAs/GaAs. In these heterostructures, there exist more than two different atomic bonds since more than three elements are included to form these heterostructures. For example, there are two kinds of bond, In-As and Ga-As, in an InAs/GaAs system, and they have different bond-strengths. This difference in bond strengths is expected to affect not only the heteroepitaxial growth process but also the characteristics of the fabricated devices. One reported example is the difference in surface mobility between Al and Ga atoms during growth interruption. Surface Al atoms have a shorter surface diffusion length than Ga atoms since they have a stronger atomic bond with As atoms than Ga does.[1] In addition, phase separation of surface metallic atoms is reported to occur on misoriented substrates.[2] This may also arise from the difference in bond strengths. We have previously reported on the anomalous distribution of In atoms in GaAs during migration-enhanced epitaxy (MEE)[3,4] as one example of the effect arising from the difference in bond strengths.[5] In the present report, this phenomenon is studied in more detail using other experimental results, including an AlAs/GaAs system. The phenomenon can be well explained by the atomic replacement of surface metallic atoms during the growth.

## 2. Growth of InAs monolayer structures

Reflection high energy electron diffraction (RHEED) observations were performed during the growth of InAs monolayer structures, which consist of one monolayer (ML) of InAs between GaAs layers. The $As_4$ beam pressure was chosen to be comparatively low ($2.0\times10^{-6}$ Torr), and the substrate temperature was changed from 300°C to 600°C. The deposition time per MEE cycle was fixed at 2 s for both In and Ga atoms. This deposition time corresponds to the deposition of one monolayer of metallic atoms per cycle. The deposition time of $As_4$ molecules was optimized from RHEED observations to avoid depositing excess $As_4$ molecules.[4] As a result, the deposition time was short for low substrate temperatures and long for high substrate temperatures. However, the period of MEE cycle was fixed at 5 s; i.e., when an $As_4$ deposition time of 1.5 s was chosen, one MEE period was composed of 2 s of metal deposition, 1.5 s of $As_4$ deposition, and 1.5 s of annealing.

The results from RHEED observation depend largely on the substrate temperature. Typical re-

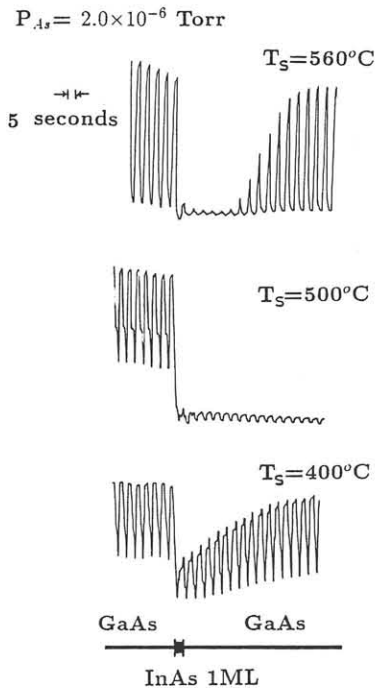


**Fig.1.** RHEED specular beam intensity change during the growth of InAs monolayer structures at 560°C, 500°C, and 400°C. The deposition times of $As_4$ molecules are 3 s, 1.6 s and 1.5 s for these substrate temperature respectively.

sults for temperatures of 560°C, 500°C, and 400°C are shown in Fig. 1. The optimized deposition times of $As_4$ molecules were 3 s, 1.6 s and 1.5 s respectively for these substrate temperatures. As soon as one monolayer of InAs was grown, the amplitude of RHEED oscillation dropped considerably, regardless of the substrate temperature. Then, the amplitude recovered as the growth continued with GaAs layers on the InAs atomic layer when the substrate temperatures were 560°C and 400°C. However, this recovery of RHEED oscillation could not be observed for 500°C even after the growth of 20 ML of GaAs.

In addition, the RHEED pattern was observed in these growths. Usually, a 4-fold pattern is observed for metallic stable surfaces and a 2-fold pattern is observed for As stable surfaces with the electron beam azimuth of [011][3]. We observed a similar change in RHEED pattern during the MEE growth of initial GaAs layers. However, after the growth of an InAs atomic layer, the 4-fold pattern did not quickly change to the As stable 2-fold pattern until the RHEED oscillation recovered, especially at 500°C.

The composition profiles of InAs monolayer structures fabricated under similar conditions were observed by secondary-ion mass spectroscopic (SIMS) analysis, with a resolution of about 10 nm. The fabricated structure is shown in Fig. 2. A 3-ML thick $Al_{0.5}Ga_{0.5}As$ was grown in the lower GaAs layer for the position reference. The measured composition profiles are shown in Fig. 3. For the Al composition (dotted curve in Fig. 3), symmetrical depth profiles were obtained regardless of the substrate temperature. The distribution of In (solid curve in Fig. 3) shows that symmetrical profiles were also obtained for the samples grown at 400 °C and 560 °C. The designed structure seems to be reproduced in these samples. However, the In profile is quite asymmetrical in the structure grown at 500°C. The comparison between the peak positions of In and Al distributions reveals that In atoms spread over a distance of 30 nm towards the surface during the growth of the upper GaAs layer. The integrated In densities were $6.3 \times 10^{14}$ and $6.5 \times 10^{14} cm^{-2}$ for the growth temperature of 500°C and 400°C, respectively. Note that these values are close to the surface site density of (100) GaAs ( $6.4 \times 10^{14} cm^{-2}$ ). A much lower integrated In density of $1.3 \times 10^{14} cm^{-2}$ was obtained for the sample grown at 560°C indicating considerable evaporation of In atoms from the surface.

This anomalous distribution of In atoms seems to be caused by the difference in bond strengths between In-As and Ga-As. Most of the In atoms in the surface InAs atomic layer will be replaced by the subsequently deposited Ga atoms on this surface, since the Ga-As bond is stronger than the In-

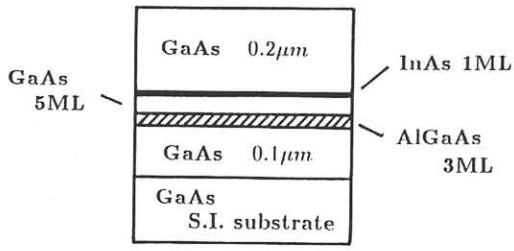


**Fig.2.** Fabricated monolayer structures for SIMS analysis.

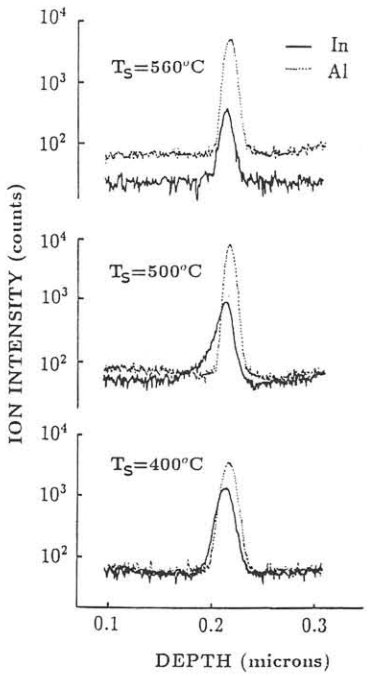


**Fig.3.** SIMS composition profiles of fabricated structures.

As bond. When this process is repeated many times, In atoms can be found at a great distance from the InAs atomic layer. Since the $As_4$ deposition time was optimized for the growth of GaAs, there was a shortage of As on the surface for the growth of InAs. Therefore, there may be a large number of In atoms on the surface which are not covered with As atoms. Since these atoms do not have stable atomic bonds with lower As atoms, they will easily be replaced by the subsequently deposited Ga atoms, which have stronger atomic bonds with As atoms. The 4-fold pattern in RHEED observation may be dominant after the growth of 1 ML of InAs from this origin.

The critical temperature of In-Ga replacement is considered to be 400°C-500°C. At 560°C, the surface In atoms begin to evaporate. Therefore, replaced In atoms easily evaporate from the surface, so we cannot observe an anomalous In distribution by SIMS analysis, which has a finite resolution.

Surface segregation of group III atoms during MBE growth of InGaAs, GaAlAs and InAlAs has been studied by AES and XPS analyses[6]. A surface enrichment due to the segregation has been found with the tendency of In>Ga>Al. That result also seems to arise from the replacement of group III atoms.

## 3. Self Organization of Atomic Layer Superlattices

In order to confirm the replacement of In by Ga at 500°C, an $In_{0.5}Ga_{0.5}As$ layer was grown on a (100) InP substrate at 500°C by MEE with the simultaneous deposition of 1ML In and 1ML Ga per one cycle. Figure 4 shows this deposition sequence. A small amount of As deposition, with a pressure ($P_0$ in Fig.4) of $2.4 \times 10^{-6}$ Torr was introduced during the period of group III element deposition in order to suppress As evaporation from the underlying As plane as with the case of FME[7]. During As-layer formation, the $As_4$ pressure (P in Fig.4) was $1 \times 10^{-5}$ Torr.

Atomic replacement in the surface neighboring layers will cause the periodicity along the growth direction with the period of 2 ML. Figure 5 shows the X-ray diffraction spectrum of the grown layer. The layer thickness was $1\mu m$. The satellite peaks corresponding to the periodicity along the growth direction are clearly observed at (100) and (300) for both samples. This result indicates that the desired superlattice structure is obtained and that replacement occurs in every MEE cycle between the first and the second surface atomic layers in an InAs/GaAs system.

An $Al_{0.5}Ga_{0.5}As$ layer was also grown on a (100) GaAs substrate at 630°C using a similar deposition sequence. 1ML of Ga and 1ML of Al were

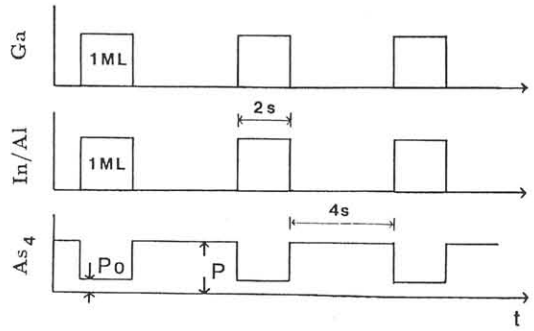


**Fig.4.** The molecular beam supply mode for the growth of a self-organized atomic layer superlattice.

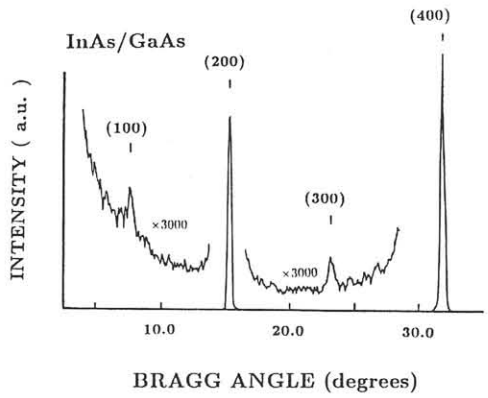


**Fig.5.** X-ray diffraction spectrum of $In_{0.5}Ga_{0.5}As$ by codeposition of In and Ga in MEE at 500°C.

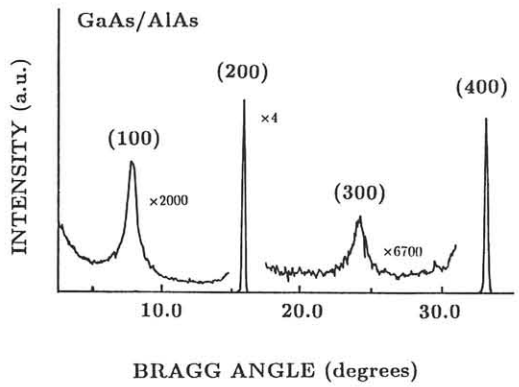


**Fig.6.** X-ray diffraction spectrum of $Al_{0.5}Ga_{0.5}As$ by codeposition of Al and Ga in MEE at 630°C.

deposited simultaneously per MEE cycle. The $As_4$ pressure was $1\times10^{-6}$Torr during group III element deposition ($P_0$ in Fig.4) and $8\times10^{-6}$Torr during As layer formation (P in Fig.4). Figure 6 shows the X-ray diffraction spectrum of this layer. Two satellite peaks are also observed with this structure. This indicates that atomic replacement can also occur in a GaAs/AlAs system.

## 4. Conclusion

We fabricated InAs single monolayer structures between GaAs layers at several growth temperatures by MEE. RHEED observations during growth showed that the recovery of RHEED specular beam intensity oscillation after InAs monolayer growth required more than 100 monolayers of GaAs over-growth only at 500°C. SIMS analysis indicated that the distribution of In atoms is quite asymmetrical with a prominent gradual slope toward the surface. This phenomenon can be explained in terms of metallic atom replacement on the growing surface. The $In_{0.5}Ga_{0.5}As$ and $Ga_{0.5}Al_{0.5}As$ layers were grown with a deposition sequence in which the total deposition rate of group-III elements was 2 ML per cycle. X-ray diffraction analysis showed that the grown layer had an atomic layer superlattice structure.

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