

## Invited

## Surface Process in Migration—Enhanced Epitaxy

Yoshiji Horikoshi

NTT Basic Research Laboratories

Musashino-shi, Tokyo 180 Japan

Migration-enhanced epitaxy has proved useful in investigating atomic processes during epitaxial growth. RHEED observation during growth of GaAs revealed that the migration distance of Ga atoms was considerably enhanced by migration-enhanced epitaxy. Thus, atomically flat AlGaAs-GaAs heterojunctions were successfully grown at low growth temperatures. At high growth temperature, evaporation of As<sub>2</sub> takes place during Ga deposition duration, which creates As-vacancies in the vicinity of the growing surface. The defect centers based on these vacancies deteriorate photoluminescence characteristics. This problem was found to be solved by applying a supplementary As<sub>4</sub> beam during Ga deposition duration.

## 1. Introduction

Enhanced surface migration is essential to the growth of high quality epitaxial layers. In the growth of III-V compound semiconductors, surface migration is enhanced by supplying group III atoms to the growing surface in the absence of group V atoms or molecules [1]. This greatly lengthens the lifetimes of isolated group III atoms, which are quite mobile on the growing surface, resulting in these atoms migrating a large distance during growth. Migration-enhanced epitaxy (MEE) is based on this characteristic. MEE has proved useful for growing flat GaAs-AlGaAs heterojunctions and for lowering their growth temperatures. RHEED observation revealed that a flat growing surface is maintained during MEE even when the number of Ga or Al atoms deposited per cycle is not exactly adjusted to the number of surface sites ( $N_0$ ) [2].

At high temperatures, the lifetimes of isolated Ga atoms are large enough to create flat growing surfaces even using a conventional MBE if the growth condition is carefully optimized. Therefore, the effect of MEE would be less pronounced at high growth temperatures. In addition, GaAs-AlGaAs quantum wells grown at high temperatures ( $\geq 550^\circ\text{C}$ ) often exhibited defect-induced photoluminescence [3]. This problem is easily solved by applying a supplementary As-beam during Ga deposition whose intensity is much less than those needed to sustain the growth.

This paper reports on the investigation of surface migration mechanism by studying growth on singular and vicinal (001)GaAs planes. To demonstrate the effect of migration-enhanced epitaxy, photoluminescence characteristics are described for GaAs-AlGaAs single quantum wells grown by migration-enhanced epitaxy. Effect of high temperature growth is also discussed.

## 2. Migration of surface adatoms in MEE

An important question concerning MEE is whether the surface migration distance is really enhanced during growth. To demonstrate the enhancement of migration distance, GaAs was grown on singular and vicinal (001) surfaces. In this experiment, the number of Ga atoms deposited per cycle was fixed at half the number of surface sites, i.e.,  $N_{\text{Ga}} = 0.5N_0$ . Two cycles of deposition, therefore, gave a complete GaAs monolayer. The RHEED intensity oscillations observed on singular and vicinal (001) planes are illustrated in Fig. 1. When a singular (001) substrate was used, modulated RHEED oscillation was obtained. The RHEED intensity increased in every other cycle. This is because in the first cycle, 50% of the surface was covered by GaAs islands. The RHEED intensity was therefore low because the surface was rough. In the succeeding cycle, however, the surface roughness formed in the previous cycle disappeared and a flat surface reappeared. The modulation of RHEED intensity oscillation therefore evidences 2D nucleation growth.

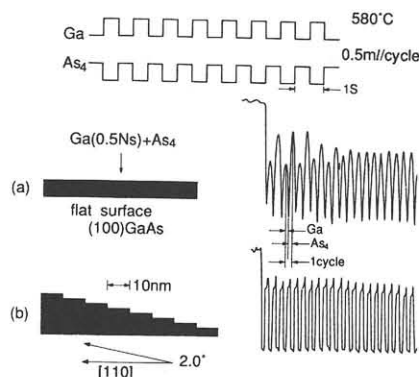


Fig. 1. RHEED specular beam intensity variation during MEE growth of GaAs on singular and vicinal (001) surfaces when  $N_{\text{Ga}} = 1/2N_0$ : (a) (001) singular surface (b) surface  $2^\circ$  off toward the (110) direction (at  $580^\circ\text{C}$ ).

When the substrate was tilted by  $2^\circ$  in the  $[110]$  direction (hereafter called the A-surface), however, no modulated oscillation occurred. This indicates that step-flow growth took place. In other words, the migration distance was larger than 10 nm, the average spacing between the atomic steps in this case. A similar result was obtained for a  $2^\circ$  misorientation in the  $[\bar{1}10]$  direction (hereafter called the B-surface) instead of the  $[110]$  direction. It is very important to note that the RHEED oscillation behavior is quite different for A-surfaces and B-surfaces. For the A-surfaces, the step-flow growth was dominant at substrate temperatures ( $T_s$ ) higher than  $540^\circ\text{C}$ , whereas for the B-surface step-flow growth occurred at  $T_s \geq 480^\circ\text{C}$ . These  $T_s$  values are much lower than those in MBE, indicating a considerable enhancement of migration distance in MEE.

Similar experiments not shown here were also performed for the B-surfaces with a  $0.5^\circ$  misorientation, which corresponds to an average spacing of 32 nm. But because no modulated oscillation was observed, the

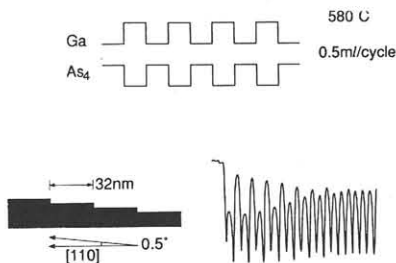


Fig. 2. RHEED specular beam intensity variation during MEE growth of GaAs at  $580^\circ\text{C}$  on a wafer  $0.5^\circ$  off (001) toward the  $[110]$  direction ( $N_{\text{Ga}} = 1/2 N_s$ ).

migration distance in the  $[\bar{1}10]$  direction must have been more than 32 nm. When the  $0.5^\circ$  misorientation was in the  $[110]$  direction (A-surface), a modulated RHEED oscillation was again observed, as shown in Fig. 2, indicating a dominant 2D nucleation growth. This result implies a longer migration distance on the B-surface than on the A-surface. This observation is well understood by considering the fact that the chemical nature of the steps in the  $[110]$  direction is completely different from that in the  $[\bar{1}10]$  direction. In fact, the steps in the  $[110]$  direction seem to have a very low probability of trapping Ga atoms [4].

To determine the effect of Ga migration, annealing experiments were performed for the A-surface with  $0.5^\circ$  misorientation. One typical result is shown in Fig. 3 for the annealing time of 2 s. The annealing was performed after the Ga and As deposition according to

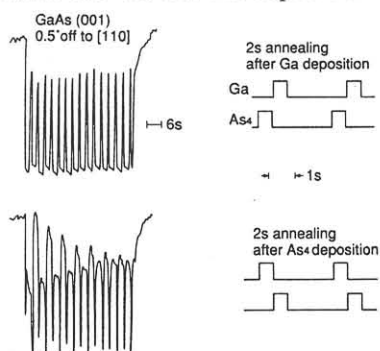


Fig. 3. Effect of 2-second annealing in the deposition sequence shown in Fig. 2. Modulation oscillation amplitude is much reduced when anneals after Ga deposition.

the sequence shown in the inset. When the annealing was done after Ga deposition, the modulated RHEED oscillation disappeared very quickly as the annealing time increased. However, with annealing after As deposition, which corresponds to interrupted MBE growth [5], no discernible change was observed in the RHEED oscillation. These results clearly indicate that step-flow growth is made possible even on the A-surfaces with  $0.5^\circ$  misorientation by surface annealing after Ga deposition.

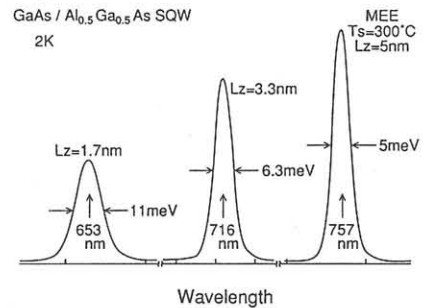


Fig. 4. Photoluminescence spectra (measured at 2K) of GaAs- $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$  single quantum wells grown by MEE at  $300^\circ\text{C}$ .

### 3. Photoluminescence characteristics of GaAs- $\text{AlGaAs}$ quantum wells

GaAs- $\text{AlGaAs}$  single quantum-well structures were grown by MEE at  $300^\circ\text{C}$ . Figure 4 shows the low-temperature spectra for single quantum wells with well widths of 1.7, 3.3, and 5.0 nm. Each single quantum well was sandwiched between a 500-nm-thick  $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$  layer grown directly on a GaAs substrate, and a 200-nm-thick upper cladding layer with the same alloy composition. The photoluminescence intensity of each spectrum is much higher than those observed in single quantum wells with equivalent well widths grown by MBE at  $580^\circ\text{C}$ .

GaAs- $\text{AlGaAs}$  single quantum wells grown at high temperatures, however, exhibited broader and less intense photoluminescence than did those grown by conventional MBE. In addition, new emission band appeared in the lower energy region of the  $n=1$  electron-to-heavy-hole transition [3]. This lower energy photoluminescence is probably caused by the defects associated with As-vacancies created during MEE growth. At temperature above about  $550^\circ\text{C}$ , the As-stable (001) GaAs surface can easily lose As atoms by evaporation of  $\text{As}_2$  during Ga deposition, because the As-cell shutter is closed during this deposition.

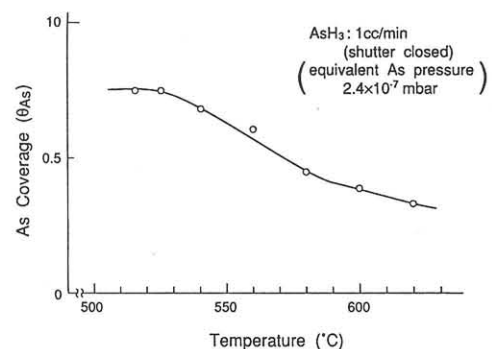


Fig. 5. As-coverage as a function of substrate temperature when the  $\text{AsH}_3$  cracker cell shutter is closed. The background  $\text{As}_2$  pressure was estimated to be  $2.4 \times 10^{-7}$  mbar.

Figure 5 demonstrates the surface coverage of As ( $\theta_{As}$ ) as functions of substrate temperature.  $\theta_{As}$  was estimated by using reflectance difference (RD) measurement [6], which is useful for estimating  $\theta_{As}$  because the RD signal intensity is sensitive to the surface chemical composition. In this experiment, the  $\theta_{As}$  on the well-defined (2x4) As-stable (001) surface was assumed to be 0.75. At about 540 °C, the growing surface begins to lose As atoms and coverage decreases from its original value of 0.75. Here, the background  $As_2$  pressure was estimated to be  $2.4 \times 10^{-7}$  mbar. Although this value is about two orders of magnitude larger than the equilibrium vapor pressure of  $As_2$  at 580 °C [7],  $As_2$  evaporation from the surface is not surprising because, since the equilibrium  $As_2$  vapor pressure is a pressure in equilibrium with the mixed phase of Ga and GaAs, the solid GaAs could contain an extremely high concentration of As vacancies. Therefore, a supplementary As deposition is needed in the Ga deposition duration of each MEE cycle to suppress the evaporation of  $As_2$  from the growing surface.

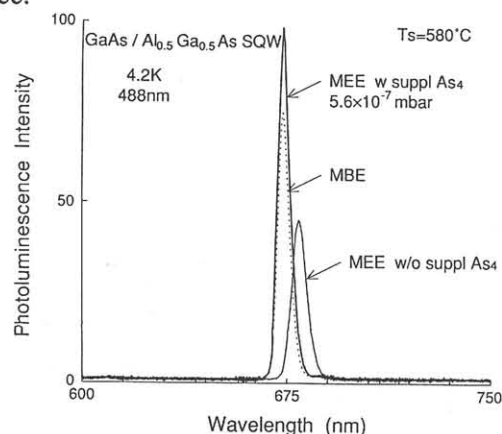


Fig. 6. Photoluminescence spectra of GaAs- $Al_{0.5}Ga_{0.5}As$  single quantum wells grown by MEE at 580°C with and without a supplementary As beam during Ga deposition. The result of MBE grown quantum well is shown for comparison.

Figure 6 shows low-temperature (4.2K) photoluminescence spectra of GaAs- $Al_{0.5}Ga_{0.5}As$  single quantum wells grown by MEE at 580°C with and without a supplementary  $As_4$  beam during the Ga deposition duration. The spectrum for the MBE grown sample is also shown for comparison. The well thickness is 10 monolayers (2.8 nm) for all samples. The sample grown by MEE without a supplementary  $As_4$  beam showed broader and less intense photoluminescence than that of the sample grown by MBE under equivalent growth conditions. Applying a supplementary  $As_4$  beam during growth, however, results in a FWHM and peak intensity that are superior to those of the MBE-grown sample. The supplementary  $As_4$  beam intensity here was as low as  $5.6 \times 10^{-7}$  mbar. This value is less than one-tenth of the pressure needed to sustain the MBE growth. Such a small amount of  $As_4$  during Ga deposition makes the MEE method useful for growing high quality GaAs even at 580°C.

In Fig. 7, the results for single quantum wells grown by MEE at 660°C are demonstrated. Without the

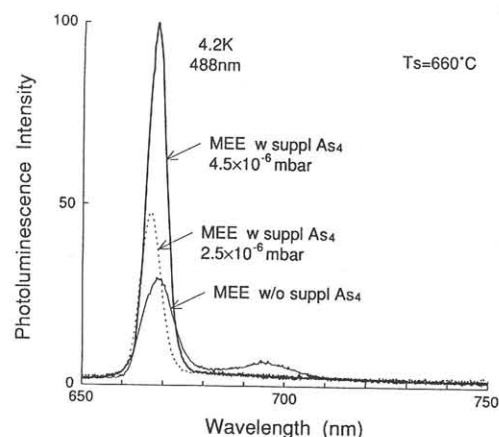


Fig. 7. Photoluminescence spectra of GaAs- $Al_{0.5}Ga_{0.5}As$  single quantum wells grown by MEE by 660°C with and without supplementary As beams.

supplementary  $As_4$  beam, the photoluminescence intensity is low and distinct broad emission band appears about 70 meV below the main emission peak. Because this band disappears when even a very weak supplementary  $As_4$  beam is applied during growth, it is probably caused by defect centers that include As vacancies. When the intensity of the supplementary  $As_4$  beam is increased, the photoluminescence peak intensity increases, and reaches that of the samples grown by MBE when the supplementary  $As_4$  pressure is  $4.5 \times 10^{-6}$  mbar. This value is about one-fifths of the pressure needed to sustain the MBE growth at this temperature. The supplementary  $As_4$  is thus effective even at 660°C.

#### 4. Summary

The principle and effect of MEE are described. RHEED observation during growth of GaAs has revealed that migration distance is enhanced much more in MEE than in MBE, and that it is further enhanced by annealing the growing surface after Ga deposition. This migration-enhancement effect of MEE is expected to be much less pronounced at high growth temperatures because the migration distance of Ga atoms is already long enough to create flat growing surfaces by using conventional MBE. However, it has been shown that the effect of MEE favorably appears even at high growth temperatures by applying a supplementary  $As_4$  beam during the Ga deposition duration.

#### References

- 1) Y. Horikoshi, M. Kawashima, and H. Yamaguchi, *Jpn. J. Appl. Phys.* 25 (1986) L868.
- 2) Y. Horikoshi, M. Kawashima, and H. Yamaguchi, *Jpn. J. Appl. Phys.* 27 (1988) 169.
- 3) C. T. Foxon, D. Hilton, P. Dowson, K. J. Moore, P. Fewster, N. L. Andrew, and J. W. Orton, *Semicon. Sci. Technol.* 5 (1990) 721.
- 4) Y. Horikoshi, H. Yamaguchi, F. Briones, and M. Kawashima, *J. Crystal Growth* 105 (1990) 326.
- 5) M. Tanaka, and H. Sakaki, *J. Crystal Growth* 81 (1987) 153.
- 6) D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, *Phys. Rev. Lett.* 59 (1987) 1687.
- 7) J. R. Arthur, *J. Phys. Chem. Solids* 28 (1967) 2257.