

Growth of AlGaAs by Atomic Layer Epitaxy using a Pulsed Vapor Phase Method

M. Ozeki, N. Ohtsuka, K. Mochizuki, and K. Kodama

Fujitsu Laboratories Ltd. Atsugi,

10-1, Morinosato-Wakamiya, Atsugi 243-01, Japan

AlGaAs epitaxial layer was successfully grown by Atomic Layer Epitaxy (ALE), where $(\text{CH}_3)_3\text{Ga}$ (TMG) and $(\text{CH}_3)_3\text{Al}$ (TMA) are supplied at different times but in series. The alloy composition was controlled with good controllability by changing the pulse durations of TMG and/or TMA. Raman spectra of AlGaAs show sharp LO and TO phonon peaks of GaAs and AlAs phonon modes, reflecting the good quality of the epitaxial. The variations of growth rate and alloy composition are explained by considering the ball-up of Ga and Al atoms and the effect of the low surface migration of Al atom.

1. Introduction

Atomic layer epitaxy (ALE) for compound semiconductors is attractive for the growth of heterostructure where the alloy composition and the doping atom can be changed at the atomic level^{1,2}). It also offers an effective tool to investigate surface kinetics of adsorbed species since surface reactions proceed more simply than the conventional epitaxy.

ALE for binary compound AB such as GaAs has been successfully achieved by the deposition of one monolayer of cation A followed by a monolayer of anion B. On the other hand, ALE for ternary compound $\text{A}_x\text{B}_{1-x}\text{C}$ is possible by simultaneously supplying the gas sources of cations A and B followed by that of anion C³). In this case, however, uncontrollable reactions between gas sources of cations A and B sometimes occur in vapor phase and/or on the substrate surface. This prevents the good controllability in growth process and the excellent surface morphology, which are peculiar to ALE.

We have developed a new ALE for ternary compounds, where cation gas sources A and B

are supplied at different times but in series. In relatively high temperature ($> 400^\circ\text{C}$), a Ga - Al exchange reaction easily takes place⁴). This enables Ga and Al atoms to intermix on the crystal surface. In this paper, the application of this technique to the growth of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ will be discussed with the growth kinetics.

2. Experimental

Growth was carried out using gas pulses of metalorganic compounds and hydride in OMVPE system. The gas source for the group III atoms was TMG or TMA and that for the group V atoms arsine gas. The following two types of gas-pulse sequences were studied (see Fig.1): (1) As pulse \rightarrow H₂ pulse \rightarrow Ga pulse \rightarrow Al pulse \rightarrow H₂ pulse (2) As pulse \rightarrow H₂ pulse \rightarrow Al pulse \rightarrow Ga pulse \rightarrow H₂ pulse. The alternating pulses of group III and arsine gas are separated by purging hydrogen gas pulses (duration of 3 s) which prevent the mixing of the reaction gases.

The growth was done in a low-pressure vertical chimney-type reactor⁵, where the carrier gas was introduced at the bottom of

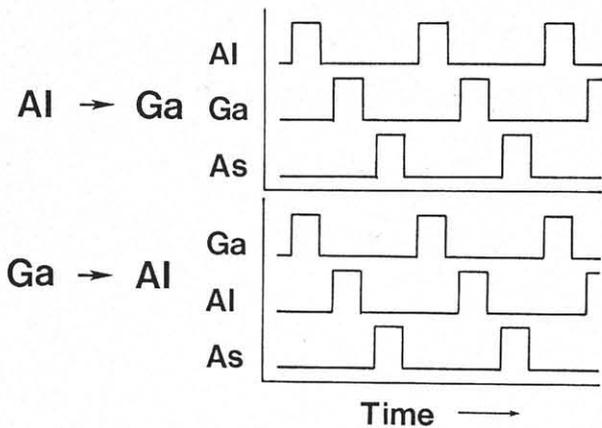


Fig.1 Gas flow sequences for AlGaAs ALE. the reactor and exhausted from the top. We used a gas handling system with a pressure-balanced vent and run configuration⁶. Due to these improvements, a gas exchange time of less than 0.1 seconds was achieved for the growth system. Hydrogen was used as the carrier gas (2000 sccm) and the vapor pressure of 20 Torr was maintained during the epitaxial growth. TMG and TMA bubbler temperatures were 3°C and 22°C, respectively. The growth temperature was 500°C.

3. Results and discussion

Figure 2 shows the variation of the growth rate of (100) GaAs and AlAs, when pulse duration of group-III source gases was changed. The growth thickness per cycle monotonously increases beyond 1 monolayer with the gas pulse duration for AlAs growth, while it tends to saturate for GaAs growth. The saturation in GaAs growth rate strongly depends upon the source gas heating process or the furnace structure. Under the growth condition where TMG was easily cracked in the stagnant layer before reaching the substrate surface, no saturation in the film thickness could be observed.

Figure 3 shows the variation of the growth thickness per gas cycle for (100) GaAs and AlAs as a function of the arsine gas pulse duration. The growth rate of GaAs decreases drastically once a film thickness of one monolayer has been reached. When arsine gas supply was short, there observed

a lot of gallium droplets on the surface. As the arsine gas supply was increased, the size and the density of the gallium droplets was decreased.

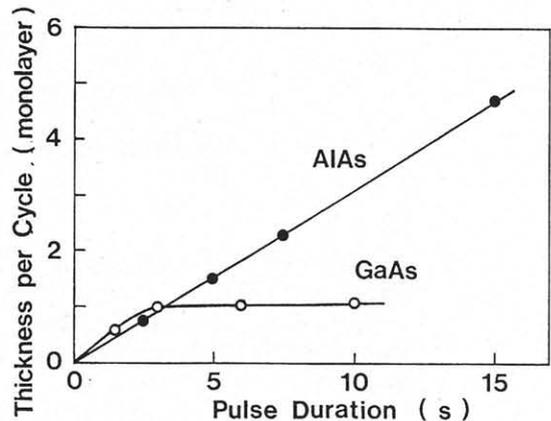


Fig.2 The growth rate variations of GaAs and AlAs. TMG: bubbler 3°C, 40sccm. TMA: bubbler 22°C, 20sccm. AsH₃: 10%, 480sccm, 10s.

In the first stage, gallium atoms chemically bond with the arsenic atoms on arsenic terminated surface, a two-dimensional gallium monolayer growing on the GaAs substrate. Once the surface is covered with gallium atoms, the second stage can begin. As the interaction between gallium and the gallium-terminated surface is weak, the gallium atoms can diffuse freely on the surface with a low diffusion energy and encounter other atoms, these forming small clusters. When a cluster grows to the

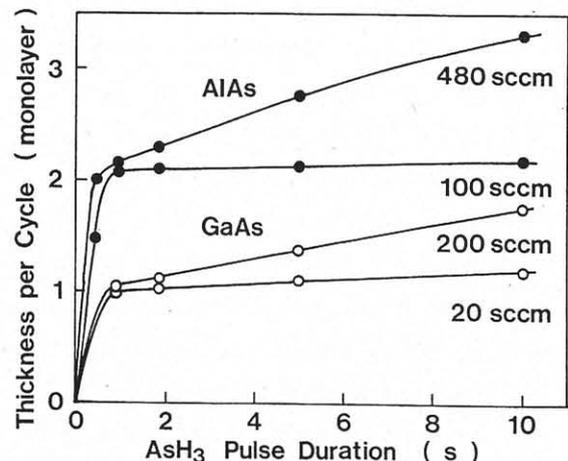


Fig.3 The growth rate variations of GaAs and AlAs. AsH₃ flow rates are described in the figure. TMG, TMA: the same as in Fig.2 except upper AlAs plots (duration 10 s).

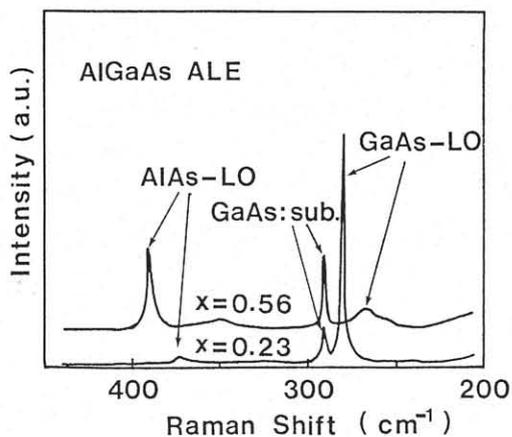


Fig.4 Raman spectra of AlGaAs grown by ALE. critical size, it forms a stable cluster whose size increases with deposition time.

When arsine gas is introduced to this gallium surface, arsenic atoms can quickly bond with the two dimensional gallium atoms and form a monolayer of a gallium arsenide. The fast gallium arsenide monolayer growth corresponds to this stage. Arsenic atoms also bond to the gallium atoms from the gallium clusters but a much longer time is needed for the formation of a GaAs layer. This corresponds to the slow growth rate once one monolayer has been formed.

In the case of AlAs, the growth rate changes at a film thickness corresponding to two monolayers, although the quick rise and gradual increase was observed in the film thickness. This can be explained by considering the atomic arrangement where the number of aluminum atoms which can be easily replaced by arsenic atoms during arsine gas period is nearly two per one arsenic atom of the AlAs.

It should be noted that the important parameter is the film thickness where the growth rate changes and not the film thickness itself that increases with the supplied arsine until the supplied Ga or Al is exhausted.

Alloy composition of AlGaAs was controlled from $x=0$ to $x=1$ with good controllability by changing the Al and/or Ga pulse duration. The AlGaAs epitaxial layer

grown under the best growth condition has mirror like surface and no gallium or aluminum droplets were present.

Figure 4 shows the Raman spectrum obtained for the AlGaAs epitaxial layer grown at 500°C. Since the film thickness is so thin (nearly 500 Å) that Raman peaks of GaAs substrate are also observed with those of the ALE AlGaAs. Sharp LO and TO phonon peaks reflect the high quality of the epitaxial layer.

Figure5 shows the variation of the AlGaAs growth rate, as arsine gas pulse duration was changed. The quick rise and the gradual increase in the film thickness was the same as for the GaAs and AlAs ALE. It should be noted that the film thickness at which the growth rate changes is larger than one monolayer of AlGaAs.

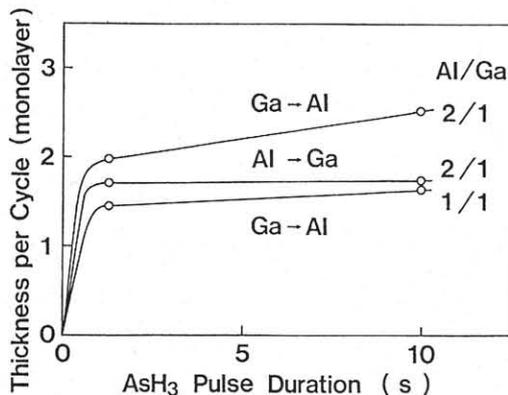


Fig.5 The growth rate variation of AlGaAs as a function of the AsH_3 pulse duration.

AsH_3 : 10% 480 sccm. TMG,TMA: the same as in Fig.2.

Figure6 shows the variations of the total film thickness, and Al and Ga contents in the epitaxial layer for Al → Ga and Ga → Al sequences as a function of TMA gas pulse duration. Here, Al and Ga contents are expressed by the unit of a monolayer of AlGaAs. In Fig. 6, TMG sufficient to grow one monolayer of GaAs was supplied and the TMA pulse durations of 3.5 and 7 second correspond to the growth of one and two monolayer of AlAs, respectively.

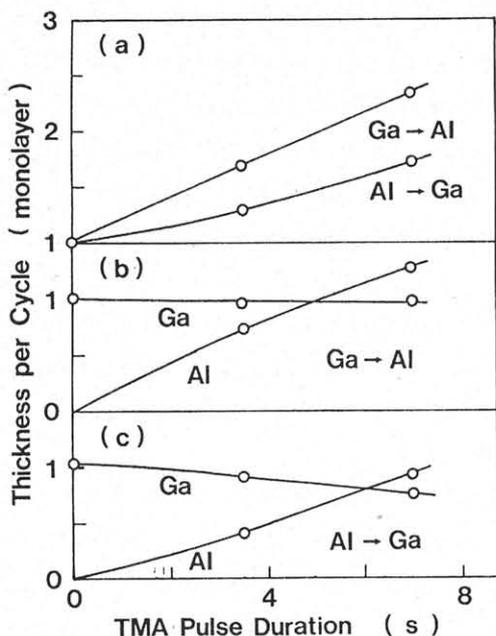


Fig.6 Variations of the thickness, and Al and Ga contents as a function of TMA pulse duration. TMG: 40sccm, 4s. TMA: 20sccm.

The epitaxial grown under the low supply of arsine gas also exhibited droplets on the surface and their density and size decreased with increasing the arsine gas pulse duration.

For both sequences, the total film thickness per gas cycle was thinner than the sum of the film thickness of GaAs and AlAs which were independently grown under the same TMA and TMG supplies. This can be explained by the balling up of the Ga and Al atoms on the surface. Figure 6(b) and (c) show that the decrease in the thickness comes from the decrease of Al atoms incorporated into epitaxial film. This is quite consistent with the analysis by Scanning Auger Microprobe (SAM) which indicated that the droplets on AlGaAs surface was composed of Al metal.

The surface migration and interaction of Al and Ga atoms have important effect on the formation of clusters or metallic droplets, and hence on the growth rate of AlGaAs ALE. Al atoms on the arsenic-atom terminated surface have small diffusion length and easily forms the nucleus to be Al

droplets. This explains the smaller growth rate of the Al \rightarrow Ga sequence compared with that of Ga \rightarrow Al sequence (Fig.6).

4. Summary

AlGaAs epitaxial layer was successfully grown by ALE using TMG, TMA, and AsH₃. TMG and TMA were supplied at different times but in series. The alloy composition was controlled with good controllability by changing the pulse duration of TMG and TMA. Raman measurements show the sharp peaks associated with LO and TO phonons of AlGaAs, which reflect the good quality of the epitaxial layer. The variations of growth rate and the alloy composition were explained by considering the ball-up of Ga and Al atoms and the effect of the low surface migration of Al atoms.

Acknowledgments

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