LOW-TEMPPERATURE GROWTH CONDITIONS AND PROPERTIES OF AlGa (As) Sb ON GaSb SUBSTRATE BY LPE

S. Fujita, N. Hamaguchi, Y. Takeda, A. Sasaki

To cite this version:
S. Fujita, N. Hamaguchi, Y. Takeda, A. Sasaki. LOW-TEMPERATURE GROWTH CONDITIONS AND PROPERTIES OF AlGa (As) Sb ON GaSb SUBSTRATE BY LPE. Journal de Physique Colloques, 1982, 43 (C5), pp.C5-29-C5-38. <10.1051/jphyscol:1982505>. <jpa-00222224>

HAL Id: jpa-00222224
https://hal.archives-ouvertes.fr/jpa-00222224
Submitted on 1 Jan 1982

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
LOW-TEMPERATURE GROWTH CONDITIONS AND PROPERTIES OF A1Ga(As)Sb ON GaSb SUBSTRATE BY LPE

S. Fujita, N. Hamaguchi, Y. Takeda and A. Sasaki

Department of Electrical Engineering, Kyoto University, Kyoto 606, Japan

1. Introduction. - Much attention has been given to A1Ga(As)Sb ternary or quaternary alloy semiconductor as an attractive candidate material for optoelectronic device application in a 1-μm wavelength range because of its wide variation of bandgap energy by adjusting alloy composition rate together with its close or exact lattice matching with GaSb. Investigations in laser diodes and photodetectors utilizing an A1Ga(As)Sb/GaSb heterostructure have been carried out by many authors[1-12] as an alternative to an InGaAsP/InP system. Although A1Ga(As)Sb alloy semiconductors have intensively grown by a liquid-phase epitaxial (LPE) technique, problems still remain with the growth of device-quality single crystal and also there still remain unresolved in electrical and optical properties of these epilayers[13]. In order to make the best use of high potential of A1Ga(As)Sb/GaSb system as a material for long wavelength optoelectronic devices, it is of great importance to investigate further the growth conditions for high-quality epilayers imperative for a high device.
In this paper, we describe experimental results of LPE-grown AlGaSb or AlGaAsSb on a GaSb substrate. The relationship between the growth temperature and the epilayer properties is investigated by changing the temperature over a wide range from 600 to 400°C. In particular, we demonstrate that the interface instability between the epilayer and the substrate can be effectively suppressed by lowering the growth temperature even in the epilayer with a high Al composition rate. Arsenic addition to ternary layer releases the interface instability: at the same growth temperature, the largest Al composition rate becomes higher in AlGaAsSb quaternary epilayer than in AlGaSb ternary epilayers which can be grown without the instability. Further, it is described that carrier concentration is significantly reduced by decreasing the growth temperature. Finally, it is also reported that two distinct acceptor levels are found to exist in the epilayers by photoluminescence measurements.

2. Experimental procedures.- The epitaxial layers of the ternary or the quaternary alloy semiconductors are grown from Ga-rich solution on (111)-B oriented GaSb substrates using a sliding boat technique in a Pd-diffused hydrogen stream in horizontal furnace. The sliding boat used in this work is composed by a double-bin type crucible which enables us to supply fresh and almost thermal equilibrium melt to a substrate[13]. The GaSb substrate (MCP Electronics LTD.) are both of n-type (Te doped, n=6x10^17 to 1x10^18 cm^-3 ) and p-type (Zn doped, p=3x10^18 cm^-3 ). These substrates are etched in a solution of HF:HNO3:CH3COOH=1:19:30 (F solution) or Br2 in methanol and subsequently rinsed in deionized water or methanol, prior to loading to the furnace. The preparation procedures for the substrate are important for growing uniform and smooth epilayers. The substrate orientation must be accurate within ±0.2° to obtain an as-grown mirror-like epilayer. The best results are well reproduced with thorough rinse by pure methanol after a final etching of the substrate in the F solution. The raw materials for the melt are 7N-Ga, 5N-Al, 6N-Sb, and a GaAs polycrystal. The dew point at the downstream of the growth tube is lower than -76°C during the growth runs. The heating cycles for the growth are schematically illustrate in Fig. 1. The cycle A is for the melt baking of Ga and Sb, where the temperature is kept at 700°C for 3 to 24 hrs. After the baking, Al and GaAs are added to the melt and the substrate is loaded to the boat (cycle B): For a high temperature growth (TG > 500°C), the growth solution is heated to a temperature slightly above the growth temperature and maintained at this temperature for 30 min to equilibrate the melt, and then the growth is started (Fig. 1 (a)). For a low temperature growth (TG < 500°C), a heat cleaning cycle C for the substrate at 550°C for 1 hr has to be added before the growth in order to obtain smooth and uniform alloy epilayers (Fig. (b)). A cooling rate of 0.2 to 0.3°C/min is used and the thickness of the epilayers is about 0.5 to 15μm depending on the growth interval.

3. Results and discussions.

3.1 Relationship between epilayer growth and substrate preparation process.
In LPE technique, good "wetting" between a melt and a substrate is needed for uniform and smooth morphology together with thickness control of a grown layer. The "wetting" is greatly dependent on a substrate surface condition just prior to the growth.

We investigate the influence of substrate preparation condition and growth temperature on the "wetting" or the growth rate of AlGaSb ternary alloy epilayer.

As shown in Table I, the apparent
growth rate for Al0.39Ga0.61Sb grown at Tg=500°C exhibited remarkable dependence on the GaSb substrate preparation process. The growth rate is seen to be reduced with decreasing the resistivity of the water used as a final rinse solution for the substrate. At Tg=400 and 450°C, Al0.39Ga0.61Sb was not grown at all unless the heat cycle C mentioned in the previous section was introduced prior to the growth regardless of the process subjected to the substrate, whereas no significant difference in the growth rate for Al0.39Ga0.61Sb was observed at a higher Tg than 550°C with various kinds of the final rinse for GaSb.

Judging from the above experimental observation, the surface of the GaSb substrate would be presumably covered by some undesirable thin layer of which thickness is dependent on the quality of the water, which gives great influence on the "wetting" or the apparent growth rate of the epilayer. Although it is still unrevealed whether the thin surface layer covering the substrate surface is formed by an oxide or other materials, the fact that the growth rate at a high Tg is less sensitive to the final rinse solutions for GaSb used in this experiment suggests that the thin surface layer can easily be removed by thermal etching at a high temperature just before the melt comes into contact with the substrate, which leads to a good "wetting" of the melt with a substrate. However, the surface morphology of the epilayer was uniform and smooth when using pure methanol or water with ρ > 15Ω-cm as a final rinse solution for the substrate. Thus, the thickness control of the epilayer with excellent morphology becomes easier in the LPE growth at a lower temperature.

3.2 Low-temperature growth of AlGaSb and AlGaAsSb

The low-temperature growth of AlGa(As)Sb has been found to be very effective to reduce the concentration of background impurities or defects[9, 13, 14] and further to suppress the interface instability between the alloy epilayer and the GaSb substrate[13]. Calculations and experiments for the phase diagram of the ternary alloy semiconductors have been carried out by several authors[15-19]. However, there are only a few reports[13, 14, 17] on experimental studies for low-temperature LPE grow-
th of these ternary and quaternary alloy semiconductors. In order to obtain high-quality heteroepitaxial layers of these materials, the LPE growth was performed at $T_G$ below 540°C.

Experimentally determined solidus isotherms in AlGaSb system grown at 400 and 540°C are shown in Fig. 2. These experimental results are in good agreement at a low $x_{Al}$ region with the calculated results based on a simple solution model reported by Cheng et al.[17]. Figure 3 shows the relationship between Al atom-fraction in solidus phase and in liquidus phase, i.e., Al distribution coefficient. It is seen that Al distribution coefficient, $X_{Al}^{S}/X_{Al}^{L}$, in AlGaSb at $T_G=400^\circ C$ decreases from 50 to 15 with increasing $X_{Al}$ from 0.001 to 0.55. The raising of $T_G$ to 540°C reduces $X_{Al}^{S}/X_{Al}^{L}$ by approximately one half within $X_{Al}$ employed in this work. The growth rate decreases with increasing $X_{Al}$ at both $T_G$'s, as shown in Fig. 4. In particular, a submicron AlGaSb epilayer can be easily reproduced by decreasing $T_G$ to 400°C.

Figure 5 indicates the growth temperature dependence on the growth rate of $Al_xGa_{1-x}Sb$ with $x=0.38 - 0.40$.

It is well known that crystal instability is often observed at the interface in a heteroepitaxial growth of AlGaSb on GaSb[13, 17, 20, 21]. We observed that the low-temperature growth of AlGaSb is very effective to suppress the interface instability and that the As addition to the melt, i.e., the quaternary epilayer growth leads to uniform straight interface. The Al composition rate $x$ in $Al_xGa_{1-x}Sb$ beyond which the interface becomes nonuniform was extended from 0.47 to 0.84 by lowering $T_G$ from 600 to 400°C. Figure 6 shows a typical example of $Al_{0.84}Ga_{0.16}Sb$ layer surface and cleaved cross section where $T_G$ is 400°C. No interface instability is observed. Relationship between the interface instability and the growth temperature as well as the As addition is shown in Fig. 7 where one can clearly see that the instability is able to be suppress by lowering $T_G$ or by the As addition even in the heterogeneous growth of these alloys with a high Al composition rate. The avoidance of instability is essentially important in wide-gap heterojunction device applications. In general, interface instability is caused by constitutional supercooling phenomenon[22].
Assume that the instability in the present experiments is due to the supercooling phenomenon. In order to avoid the supercooling, a criterion must be followed that required $GL/v$ be greater than a certain value\[22\], where $GL$ is the temperature gradient in the liquidus at the interface and $v$ the growth velocity. If $GL$ is assumed to be constant in each growth run in Fig.7, a value of $GL/v$ would be increase with reducing $T_G$ or with the As addition since the growth rate is significantly decreased by lowering $T_G$ or by the As addition, which agrees with the requirement for suppression of constitutional supercooling. At the same $T_G$, on the other hand, the growth rate decreases with increasing Al composition rate as shown in Fig. 4. However, the instability is easy to occur in the growth at higher Al composition rates. Therefore, it cannot be explained only in terms of the growth rate. Since the critical value of $GL/v$ depends on the liquidus slope, the liquid concentration, the distribution coefficient and the diffusion constant at the interface of each component, it is further required to take these factors into account for the interpretation of the instability phenomenon.

The As composition rate is quite limited in the AlGaAsSb quaternary alloy system, which results in difficulty in growing AlGaAsSb lattice-matched with GaSb. This would be due to low solubility of As into the liquidus phase\[2\] or due to a miscibility gap in a Ga-As-Sb system\[23, 24\]. Therefore, AlGaAsSb with a high As composition lattice-matched with GaSb cannot be grown at a low growth temperature\[9, 19\]. However, even in the quaternary epilayer lattice-mismatched with GaSb, we were able to reproducibly grow the excellent morphological epilayer with a high Al composition rate, which is free from the interface instability as shown in Fig. 8.

Figure 9 shows the $T_G$ dependence of the As composition rate in solidus phase of AlGaAsSb. At $T_G=400°C$, the maximum As composition rate $y$ in Al$_{0.4}$Ga$_{0.6}$As$_y$Sb$_{1-y}$ is estimated around 0.0045. Al$_{0.39}$Ga$_{0.61}$As$_y$Sb$_{1-y}$ with $y=0.025\sim 0.03$ lattice-matched with Al$_{0.07}$Ga$_{0.93}$Sb was reproduced by raising $T_G$ up to 540°C as shown in Fig. 10. However, the increase in As atom fraction in liquidus phase leads to irregular variation in the lattice constant of the quaternary layers, which is probably caused by the miscibility gap of this quaternary system\[2, 24\]. Since the growth rate of the quaternary epilayer is significantly decreased with the As composition rate in liquidus phase as indicated in Fig. 11, we can successfully reproduce the submicron (<0.5 μm) quaternary layers, which is very useful for double heterojunction applications.
Fig. 9. Growth temperature dependence of the As composition rate in solidus phase in Al$_x$Ga$_{1-x}$As$_y$Sb$_{1-y}$ quaternary epilayers. The results by Motosugi et al.[19], and Law et al.[2] are also indicated for comparison.

3.3 Electrical and luminescent properties of AlGaSb.

In order to investigate the electrical properties of epilayers, the Hall measurements have been carried out by a p-n junction separation technique because of a semi-insulating GaSb substrate unavailable. The undoped AlGaSb epilayers show p-type conduction regardless of $T_G$'s employed at present work. However, hole concentrations are significantly reduced by about two orders in magnitude by lowering $T_G$ from 600 to 400 °C as shown in Fig. 12. Al$_{0.4}$Ga$_{0.6}$Sb$_y$ epilayer at $T_G$=400°C is seen to have a typical value of $p$=8x10$^{15}$cm$^{-3}$ at room temperature. Temperature dependence of hole concentration of the epilayers at $T_G$=400 and 536°C is shown in Fig. 13. These results could allow us to evaluate acceptor levels, the acceptor and the compensating donor concentrations by computer analyses. Although attempts to estimate these material parameters of the epilayers by the computer analyses have been made, it is found to difficult to evaluate the reasonable values of the parameters because of remarkable influence on the Hall measurements at a high temperature region of leakage current of p-n junction used electrical separation between the epilayers and the substrates. A rough estimation from the data at a low temperature region gives a value of 25 to 30 meV for an acceptor level.

In undoped p-type GaSb, a model of doubly-ionizable acceptor whose origin is connected with an intrinsic Sb vacancy has been reported[25]. It has been indicated, on the other hand, that by reducing $T_G$ undoped AlGaSb or GaSb epilayers exhibit n-type[9, 14, 26] and further residual donor concentration decreases drastically up to 2-4x10$^{13}$cm$^{-3}$ for Al$_{0.2}$Ga$_{0.8}$Sb and up to 2x10$^{13}$cm$^{-3}$ for GaSb[14, 26]. The origin of p-type conduction in our epilayers is still unknown whether it is due to intrinsic defects related to a Sb vacancy[25] or to extrinsic impurities such as Si[30]. Further experiments for obtaining high-purity epilayers are needed to elucidate the origin.
Photoluminescence (PL) measurements were made for Al$_{0.07}$Ga$_{0.93}$Sb ternary epi-
layers grown at T$_G$'s from 550 to 400°C to obtain information on impurity or defect
levels involved. A high-pressure Hg lamp with a filter or argon ion laser (1W )
for excitation source and a cooled PbS photoconductive cell for a detector were used
for the measurements.

Fig. 14 shows PL spectra measured at 77 and 4.2K in an epilayer grown at T$_G$=450
°C. At 4.2K four emission bands labelled as $I_x$, $I_1$, $I_a$, and $I_c$ can be observed at
0.873, 0.870, 0.844, and 0.815eV, respectively, while one can see two distinct emis-
sion bands of $I_q$ and $I_d$ located at 0.870 and 0.842eV at 77K, respectively.

The $I_0$ emission band at 77K varies in peak photon energy depending on the slight
difference in the Al composition rate among the epilayers grown at different T$_G$'s,
as shown in Fig. 15. However, the peak energy difference between $I_0$ and $I_d$ re-
mains almost unchanged among the epi-
layers: the value is about 27meV. Fur-
ther, the intensity of $I_d$ with respect
to that of $I_0$ tends to decrease at lower T$_G$'s which lead to decrease in the
acceptor concentration.

From these results, the $I_0$ emis-
sion band may be arised from direct
transition from electron in the conduc-
tion band to hole in the valence band, deducing from data of temperature dep-
endence of bandgap for GaSb together with Al composition dependence of that
for the ternary alloy system[28-30].
And in addition, $I_d$ can be ascribed to radiative recombination due to a transi-
tion of free electron into an accep-
tor level $E_A$ located at about 27meV
above the valence band. This value
is interpreted with the acceptor level
deduced from the electrical measure-
ments.

Fig. 12. Growth temperature dependence
of hole concentration of p-AlGaSb layer.
Solid square is after Gautier et al.[32].

Fig. 13. Temperature dependence
of hole concentration of p-AlGaSb
at T$_G$=400 and 540°C. Rapid in-
crease in hole concentration is
due to leakage current from p-n
junction at high temperatures.

Fig. 14. PL spectra at 77 and 4.2K of an
Al$_{0.07}$Ga$_{0.93}$Sb epilayer grown at 450°C.
PHOTON ENERGY (eV)

0.900 0.850 0.800

- ! - >
t V z r f W U z W S:

Table I1 shows the summary of the peak energies and the proposed mechanisms of each line observed by the PL measurements.

At 4.2K, the emission intensity of I1 band increases strongly with increasing the excitation intensity but no displacement of the emission peak energy is observed, and in addition, the emission intensity of I1 is strongly dependent on Tg: the I1 intensity of an epilayer grown at Tg=400°C is relatively stronger than that of an epilayer at Tg=550°C whose carrier concentration is higher by about one order in magnitude than that grown at Tg=400°C. Further, the I1 intensity is drastically reduced at above 4.2K. These observations strongly suggest that the I1 band is due to radiative recombination from exciton bound to neutral acceptor, considering that the epilayers are p-type. Similar carrier concentration dependence on emission intensity of bound exciton complex to our results has been observed in GaAs[31]. The relatively broad emission band of I1 would be ascribed to fluctuation of energy state due to perturbed disorder arrangement of the constituent group-III atoms in the lattice.

The binding energy of free exciton, Eex for Al0.07Ga0.93Sb can be estimated to be Eex=3meV by extrapolating physical constants for each binary compound[23]. If the highest energy emission band Ix located at 0.873eV is assumed to be due to free exciton emission, the band gap energy Eg at 4.2K for the alloy epilayer is evaluated to be 0.876eV which is smaller by about 15meV than that deduced from PL data reported by Allegre et al.[28]. This relatively large discrepancy in the energy gap is not clear, but it would be caused by the possibility that the Al composition rate determined by an X-ray diffraction technique slightly differs from the rate of the actual epilayer. Using EA, Eex, and Eg thus estimated, we can calculate the binding energy of I1. From an effective mass arguments developed by Hopfield[27], the photon energy emitted by radiative recombination of exciton bound neutral acceptor, E(A0,X) is given by a following equation: E(A0,X) = Eg - Eex - 0.06EA where the electron mass, me and the hole mass, mh for Al0.07Ga0.93Sb is taken as 0.0476m0 and 0.479m0[23] (m0 is free electron mass), respectively. Then, the calculated value for E(A0,X) is 0.871eV which is in good agreement with the peak energy of I1.

As for Ia observed at 4.2K, we can assign it as the D-A pair emission because the emission peak position is slightly displaced to higher energy as the excitation energy increases. Although the emission intensities of Ib among the samples is too weak to characterize the emission mechanism, it is presumably arisen from the D-A pair emission where the related acceptor is deep one with an activation energy of around 50 to 60meV. Table II shows the summary of the peak energies and the proposed mechanisms of each line observed by the PL measurements.
4. Conclusions. - The experimental results obtained in this work can be summarized in the following:

(i) The morphology and the growth rate of AlGa(As)Sb epilayers are greatly affect-
ed by the GaSb substrate preparation processes when growing at a low temperature of 400 or 450°C. A heat cleaning process at 500 or 550°C just prior to the low temperature growth gives the excellent epilayers.

(ii) Interface instability can be avoided by lowering TG. At Tg=540°C, the largest Al-composition rate for a ternary layer without the instability is around 0.64, whereas it for a quaternary layer extends to about 0.78.

(iii) Lowering the growth temperature contributes significantly to reduction in carrier concentration: p=10^18cm⁻³ at Tg=600°C whereas p=8x10^15cm⁻³ at Tg=400°C.

(iv) PL spectra of Al₀.₀7Ga₀.₉₃Sb show four emission bands at 4.2K. Iₓ at 0.873eV, I₁ at 0.870eV, Iₐ at 0.844eV, and Iₜ at 0.815eV are presumably arisen from free exciton, exciton bound to neutral acceptor, donor-shallow acceptor pair, and donor-deep acceptor pair, respectively. At 77K, band-to-band and free-to-bound recombination are dominant in the ternary epilayer.

Experiments will be further continued to obtain the high-quality epilayers imperative for optoelectronic device applications, which also enables us to elucidate bulk and surface properties of AlGa(As)Sb alloy semiconductors.

Acknowledgments. - The authors would like to thank A. Ohishi and E. Sogawa for their help on growth experiments and measurements.

References


