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GALLIUM ANTIMONIDE LPE GROWTH FROM Ga-RICH AND Sb-RICH SOLUTIONS

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Epitaxial layers of undoped p-GaSb were grown from Ga-rich and Sb-rich solutions on (111) and (100) oriented GaSb substrates. The growth temperatures ranged from 330–470 °C (Ga solution) and 635–680 °C (Sb solution). Different growth results were obtained for the two LPE processes. The layers were characterized by photoluminescence measurements at low temperatures (1.8 K). The highest purity was obtained by low temperature LPE from Ga solutions.

1. Introduction

GaSb is the only III–V compound with a relatively small energy gap [E_g = 812 meV [1]) at 1.8 K] which is always p-type when grown without doping elements. GaSb crystals mostly have been grown by the Czochralski, the zone freezing or the solution growth method using stoichiometric and nonstoichiometric melts[2–6]). The dominant acceptor is assumed to be a native defect, e.g. an Sb vacancy[7,6]) or a Ga atom on an Sb site or a more complicated defect[7]). The concentration of this defect is dependent both on the growth temperature and the composition of the solution. Van der Meulen[7]) and Plaskett[9]) found that growth from Ga-rich solutions increases the acceptor concentration. A decrease in the hole concentration can be achieved by increasing the Sb content in the melt beyond 0.5 atom fraction[3]). The phase diagram of the system Ga–Sb [10]) is shown in fig. 1. It can be seen that the growth methods are limited by the existence of the eutectic point at 0.88 atom fraction at T = 590 °C. The lowest values of hole concentrations for crystals grown from Sb-rich solutions (Czochralski or solution growth method) were[3,4]) $p \sim 3\text{–}4 \times 10^{16}$ cm^{-2}. The corresponding values for stoichiometric melts are[3]) in the range of $p \sim 8 \times 10^{16}$–2×10^{17} cm^{-3}. On the other hand, the growth temperature of LPE from Ga-rich solutions can be very much lower. This may reduce the number of non-stoichiometric native defects as well as the number of other impurities incorporated. In the case of the Czochralski method (T = 480 °C) a value of $p \sim 3 \times 10^{16}$ cm^{-3} was reached by Gouskov and coworkers[3]). Hoyo and Kuru[11]) have reduced the growth temperature of LPE from Ga-rich solutions to 405 °C and obtained p = 8.5 $\times 10^{15}$ cm^{-3}. Recently Miki et al.[12]) reported the growth of LPE n-type material at 400 °C with n = 3.8×10^{15} cm^{-3}.

In this paper the growth of high purity GaSb layers in various regions of the Ga–Sb phase diagram will be described in connection with photoluminescence measurements at low temperatures (1.8 K).

2. LPE apparatus and experimental procedure

The experience from LPE growth of high purity GaAs and InP has been that special process control is very important[13–15]). In the following we describe the corresponding conditions for GaSb LPE. For the growth experiments we used a tipping system[14])

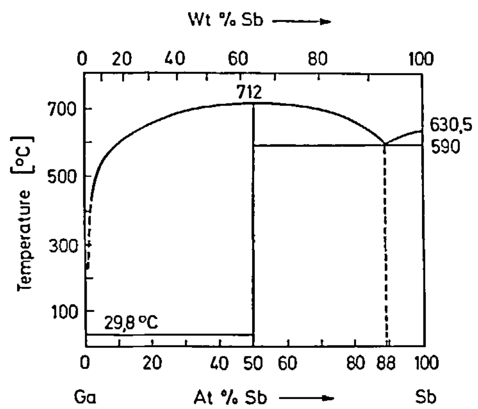

Fig. 1. Phase diagram of the system Ga–Sb.

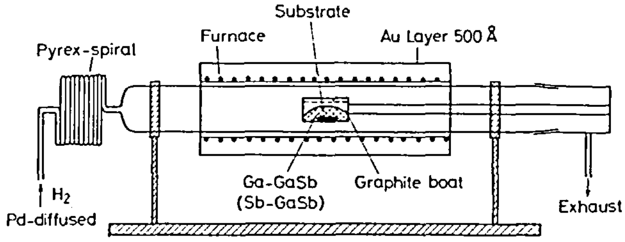

Fig. 2. Schematic drawing of the LPE apparatus with the pyrex spiral.

(schematically shown in fig. 2). The reaction tube was made of suprasil quartz, the boat for the Ga–Sb solution of high purity graphite. The tube and boat were locked together and could be rotated around the long axis for immersion and withdrawal of the substrate from the solution. To avoid air leaks we used a pyrex spiral which allowed the rotation of the tube without moving joints. The furnace was transparent[16]) in order to observe substrate and solution. The graphite boat was heated at $T = 1600$ °C under a vacuum of 10^{-6} Torr for three hours. After that the boat was loaded with 6 N Ga (Alusuisse) and baked at $T = 800$ °C in the reaction tube for 5 h under a Pd-diffused H_2 gas flow. At the end of this procedure the boat was cooled down to room temperature and the Ga was removed. The boat was then loaded again with 6 N Ga and 6 N Sb (Cominco) corresponding to the growth temperature (phase diagram). Prior to growth this Ga–Sb solution was baked at $T = 850$ °C for 5 h and with a H_2 flow rate of 15 l/h.

Essential for the beginning of the growth process is the knowledge of the tipping temperature T_K. This temperature was estimated experimentally by observing the temperature at which solid GaSb appears on the surface of the solution. By this method of determining the starting temperature, the solution was slightly supercooled at T_K. However, there are some difficulties for Sb-rich solutions which are discussed later.

Under the conditions described above, we have grown single crystal layers on (111) and (100) undoped GaSb substrates. The substrates which were available were cut 2° off orientation and were etched in a solution of 4% bromine in methanol. Prior to use the substrates were rinsed with hot chloroforme. It is important, especially for the growth at low temperatures, that the substrate does not come into contact with the air until the last cleaning step is reached. If there is any oxide layer on the substrate one has wetting problems and no uniform layer can be grown. The Ga–Sb solution was heated up 20 °C above T_K (in the case of Ga-rich solutions). The boat was agitated in order to equilibrate and homogenize the solution. The solution was tipped over the substrate at T_K. In the experimental runs on the Ga-rich side of the phase diagram T_K varied between 330 °C and 470 °C with cooling rates between 5 °C/h and 15 °C/h. For the Sb-rich side the corresponding values are T_K = 680–635 °C and 0.5–3 °C/h, respectively. After termination of the experiment, the solution was removed from the substrate by rotation of the crucible. In the case of Sb-rich solutions one should take care that no solution remains on the substrate in order to avoid the formation of eutecticum on the layer.

3. Growth results

3.1. Ga-rich solutions

For growth experiments below 480 °C the slope $d\gamma/dT$ of the liquidus curve of the Ga–Sb phase diagram is similar to that of GaAs and InP[17]) for their corresponding LPE growth range. For the cooling rates above mentioned, we got growth rates in the range of 3–10 μm/h. These growth rates are similar to those reported for GaAs[14]) and InP [15]) grown in the same type of LPE apparatus. It is difficult to make an exact comparison between these results, because the starting conditions (e.g. supercooling effects) are different.

We have grown epitaxial layers with thicknesses between 7 μm and 40 μm. Thicknesses were determined either by etching a cleavage plane or by means of a micrometer.

The layers grown on (111) A or (111) B substrates showed always a terrace structure (fig. 3). This structure is typical for LPE growth of III–V compounds and is due to misorientation of the substrate[18,19]) and due to constitutional supercooling effects[20]). In some cases, if there are any wetting problems at the substrate surface, one gets no uniform layer but wedge-shaped islands. This can be seen in fig. 4. The islands were grown on a (111) B GaSb substrate at T_K = 390 °C. The wedge angle was estimated to about 2° and may correspond to the misorientation of the substrate. LPE growth on (100) substrates can also exhibit a terrace structure besides smooth surfaces and the defects (hillocks) which are shown in fig. 5.

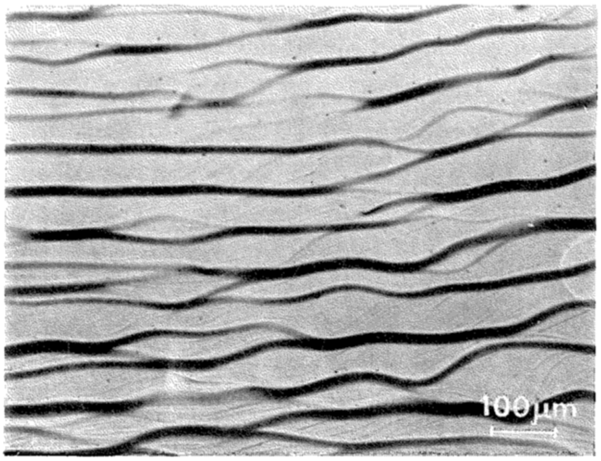

Fig. 3. Characteristic terrace structure for a layer grown on (111) B substrate; $T_K = 390$ °C.

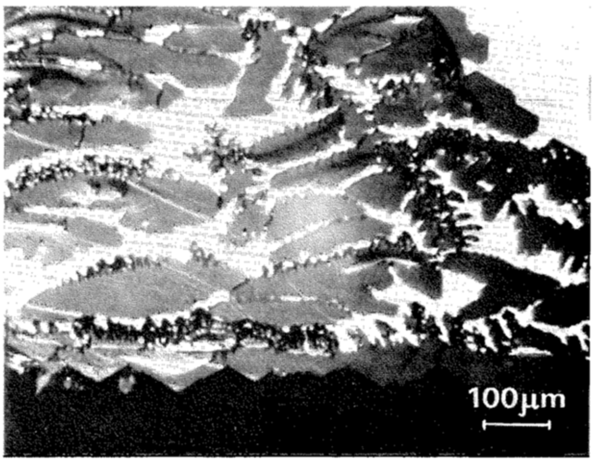

Fig. 4. Wedge-shaped GaSb islands grown on (111) B substrate; $T_K = 390$ °C.

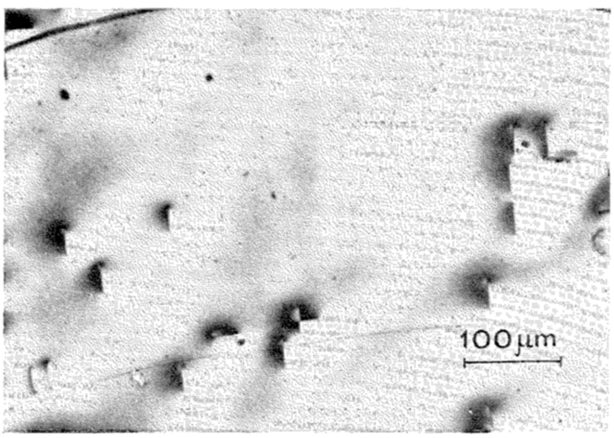

Fig. 5. Smooth layer grown on (100) substrate with 4° misorientation and some characteristic defects.

3.2. Sb-RICH SOLUTIONS

The growth results from Sb-rich solutions are different in some cases from those of Ga-rich solutions, especially the growth rates. This behaviour is mainly due to the slope of the liquidus curve of the Ga–Sb phase diagram. In a simple model, if the growth rate is expressed in $v = \mathrm{d}N/\mathrm{d}t$ (N = moles of solid GaSb, which have crystallized), one can write:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}N}{\mathrm{d}\gamma}\frac{\mathrm{d}\gamma}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t}, \qquad (1)$$

where γ is the Sb mole fraction of the solution, $\mathrm{d}\gamma/\mathrm{d}T$ the reciprocal slope of the liquidus line of the phase diagram and $\mathrm{d}T/\mathrm{d}t$ the cooling rate. Above the tipping temperature T_K the solution consists of N^0_{Ga} moles Ga and N^0_{Sb} moles Sb. If the temperature is reduced below T_K GaSb is precipitated. The mole numbers of liquid Ga and Sb in the residual solution are

$$N_{Ga} = N^0_{Ga} - N, \quad N_{Sb} = N^0_{Sb} - N. \qquad (2)$$

For thermodynamical equilibrium we can estimate $\mathrm{d}N/\mathrm{d}\gamma$ and eq. (1) can be written as:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{N^0_{Sb} - N^0_{Ga}}{(1-2\gamma)^2}\frac{\mathrm{d}\gamma}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t}. \qquad (3)$$

Now we can calculate the amount of crystallized GaSb $\Delta m/\Delta T$ per degree temperature decrease. We have done this in table 1 for three typical growth conditions. In contrast to the Ga-rich side (growth temperature 335 °C) the amount of epitaxial grown GaSb is increased by a factor of 70 for the growth from Sb-rich solutions (growth temperature 650 °C). This leads to the following conclusion:

(i) For a control of the epitaxial layer thickness (growth from Sb-rich solutions), the tipping temperature T_K should be known very accurately within ± 0.1 °C. If this is not the case, either the substrate may be dissolved

TABLE 1

Influences of liquidus line on growth parameters

Growth region (°C)	Ingot			
	N^0_{Ga} (moles)	N^0_{Sb} (moles)	$\mathrm{d}\gamma/\mathrm{d}T$ (°C)$^{-1}$	$\Delta m/\Delta T$ (mg/°C)
335 Ga-rich	0.14	2.5×10^{-4}	3.5×10^{-5}	0.95
450 Ga-rich	0.14	2×10^{-3}	2.3×10^{-4}	6.2
650 Sb-rich	2×10^{-2}	8×10^{-2}	2.0×10^{-3}	66

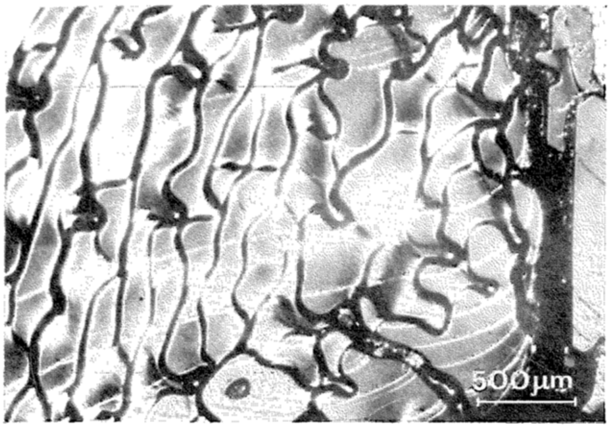

Fig. 6. (111) A layer grown from Sb-rich solution at T_K^{Sb} = 645 °C.

or too much GaSb from the solution may be precipitated on the substrate surface at the initial state of growth. The reproducibility of having the same T_K every time is also very important.

(ii) To avoid uncontrolled growth the coooling rates should be very small in comparison with the cooling rates for Ga-rich solutions.

In our experiments the stability of the furnace was ±0.25 °C. T_K was estimated by heating up the Ga–Sb solution to a temperature where some remaining GaSb was not dissolved. At this temperature, T_K^{Sb}, the solution was tipped over the substrate. T_K^{Sb} was varied between 635 °C and 680 °C. The epitaxial layer thickness ranged from 90 µm to 200 µm. Fig. 6 shows the structure of a (111) A layer grown at T_K^{Sb} = 645 °C. This structure is similar to those layers which were grown from Ga-rich solutions.

4. Photoluminescence measurements

The quality of the LPE layers was characterized by low temperature (1.8 K) photoluminescence. The crystals were excited by a Kr^+ laser (λ = 647.1 nm) which was focused to a spot of 0.25 mm diameter. The maximal light density was I_0 = 240 W/cm^2. The intensity of the light could be reduced by neutral density filters. A 0.75 m Spex monochromator was used in connection with a cooled PbS cell and the conventional lock-in technique.

Table 2 shows the energy position and interpretation of the various lines which were observed. Most of these lines can be found in other crystals[4,21,22]). However, in our LPE samples, grown from Ga-rich solutions, the

TABLE 2

Energetic position and interpretation of the emission lines at 1.8 K

h (meV)	Interpretation
810	Free exciton[4,22])
808.0–808.9	Excitons bound to donors ?[24])
804.9	Excitons bound to neutral acceptors[24,25])
803.0*	
800	
795.8	
794.6	Pair transition? (donor–isoelectronic acceptor trap transition?)[24])
781	Conduction band or donor–acceptor transition
777	(A), conduction band or donor–acceptor transition (native defect)
766	(BE-LO), LO phonon replica of line BE [4,22])
757	(B), conduction band or donor–acceptor transition[4,22])
748	(A-LO), LO phonon replica of line A [4,22])
728	(B-LO), LO phonon replica of line B [4,22])
710	Conduction band or donor–acceptor transition, second ionization level of the acceptor involved in line A [4,22])

* At these crystals the line is due to the decay of bound excitons. At other crystals however a conduction band–acceptor transition can occur at the same energy[24]).

complete near edge luminescence can be resolved in the range between 795–810 meV for the first time.

Emission spectra of two epitaxial layers grown from a Ga-rich solution (upper curve) and an Sb-rich solution are compared in fig. 7. The near gap luminescence can be attributed predominantly to the radiative decay of bound and free excitons[4,21,24,25]). GaSb also exhibits[4,21,22]) band–acceptor or donor–acceptor transitions. These transitions are associated by LO-phonon replicas. The dependence of the excitation intensity I for sample 4 (Ga-rich solution) is shown in fig. 8.

A detailed discussion of the photoluminescence results will be published later[24,25]). The line at 777.3 meV (fig. 8, upper curve) is due to the native defect in GaSb, which was shown by Van der Meulen[7]). This line at 777.3 meV is connected with the concentration of Sb in the melt: the intensity of this line decreases with increasing Sb concentration.

The resolution of near edge emission into separate lines and the half width of these lines can serve as a measure of the impurity concentration in the epi-layer. If the measured spectra are compared under these aspects with published spectra[4,21,22]) taken at samples with known impurity concentration we can estimate that the net hole concentration should be much below

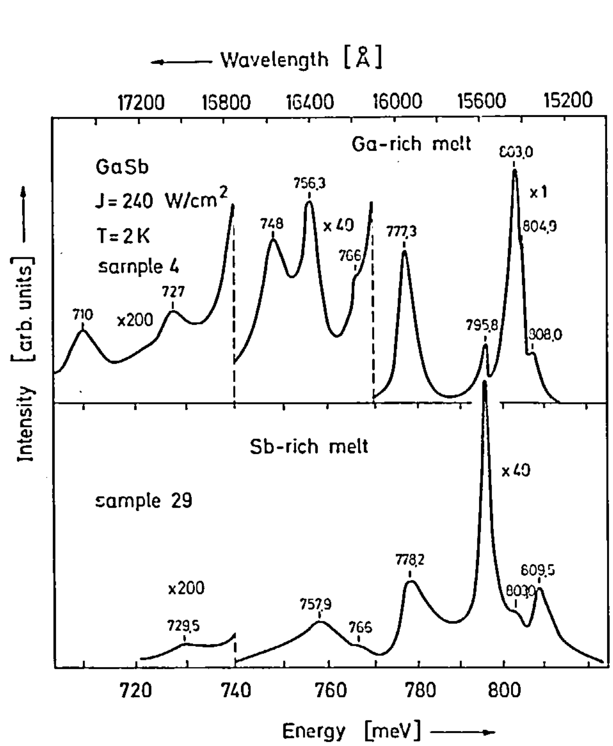

Fig. 7. Photoluminescence spectra of two epitaxial layers. Sample 4 was grown from Ga-rich solutions, $T_K = 450$ °C, and sample 29 from Sb-rich solutions, $T_K = 650$ °C.

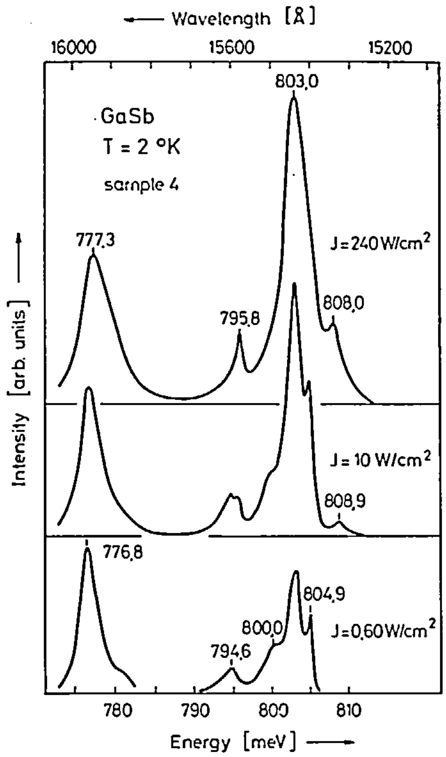

Fig. 8. Intensity dependence of emission spectra in the energy range between 770–820 meV at constant temperature (1.8 K).

3×10^{16} cm^{-3}. This is due to the growth from Ga-rich solutions with very small Sb content.

The relative intensities of the emission lines change strongly with the growth conditions (see fig. 7). For the layers grown from Ga-rich solutions, the line at 803.0 meV is the dominant emission (fig. 7 upper curve).

The photoluminescence quantum efficiency for the layers grown from Sb-rich solutions (fig. 7, lower curve) is reduced by a factor of 20 or more and the line at 795.8 meV is the strongest emission. Compared to the spectra of the layers grown from Ga-rich solutions, all lines are broader. We attribute this effect to the higher contamination with impurities which is expected for the higher growth rate and growth temperature in the case of Sb-rich solutions.

5. Conclusions

We have grown undoped GaSb LPE layers in various regions of the Ga–Sb phase diagram. The layers were p-type. The native defect is always present in the layers as can be seen from the photoluminescence spectra. For temperatures above $T_K = 600$ °C the growth from Sb-rich solutions is more favourable than the growth from Ga-rich solutions. This is due to the reduction of the Sb vacancies by increasing the Sb content of the solution. However, more important for the purity of the GaSb LPE layers is the growth temperature. Growth temperatures much below 600 °C can only be achieved with Ga-rich solutions. Thus the concentration of the native defect as well as the impurity content of the epi-layers can be reduced. We have shown this behaviour by our photoluminescence results.

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