GaSb grown from Sn solvent at low temperatures by LPE

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Abstract. The LPE growth of GaSb using Sn as a solvent has been studied in the temperature range 250-370 C and using liquid solutions covering a wide range of compositions. In order to find the growth conditions the phase diagram has been determined experimentally around the same temperature region. It is shown the Sn incorporates into the grown layers and that it behaves as an acceptor. The photoluminescence spectra of the grown layers with different Sn contents show characteristic peaks that can be attributed to different recombination processes.

1. Introduction

GaSb and its alloys with other III-V semiconductors are very interesting materials from the point of view of its potential application in several fields such as, thermo-photovoltaic cells, mid infrared lasers and photodetectors for the detection and measurements of air pollutant concentrations, for medical applications, night vision, etc. Nowadays most optoelectronic devices are grown by MBE or OMCVD techniques, however, liquid Phase Epitaxy (LPE) could, still, be an adequate growth technique for some of those devices, especially those requiring thick, high purity and/or high resistivity layers. The use of Sn as the solvent for LPE growth of these materials presents some advantages that could help to meet those requirements. The solubility of GaSb in Sn is larger than in Ga [1]. Thus it is possible to grow thicker layers from Sn than from Ga. The larger solubility also allows the growth at lower temperatures and thus to get materials with less point defects. This is very interesting since it is known that the practical use of GaSb in real devices is limited by the presence of a native complex acceptor defect [2] the concentration of native defects decreases with the temperature and it has been shown that undoped GaSb grown at low temperatures changes its conductivity to N type [3]. Low growth temperatures would offer the added advantage that techniques that involve the regrowth of epitaxial layers on complex heterostructures could be applied without disturbing noticeably the heterostructures even if they comprise very thin layers. Another advantage of using a "neutral" solvent such as Sn is that if it is used to grow different GaSb based alloys, i. e. AlGaAsSb and GaInAsSb to fabricate heterostructures by LPE, the problem of mixing the current growth solution with remaining droplets of the solution used to grow the previous layer is minimized.
2. Experimental

The growth experiments and the liquidus temperature measurements were done in a semitransparent furnace under a high purity, Pd-diffused, Hydrogen flow of 0.3 l/min. An electronic grade graphite boat of the sliding type was used in all the experiments. All the materials used to prepare the liquid solutions had a purity of 5N or higher. The liquidus temperature was determined, by observing through a microscope the liquid solution while slowly heating, as the point when the last solid disappeared. For the growth experiments the substrates were chemically polished in a solution of H2O2: HF: C4O6H6 (tartaric acid): H2O [4]. Since it is not possible to fabricate semi-insulating wafers of GaSb it is not easy to measure the free carrier concentration using standard techniques, so to determine whether Sn incorporates as a donor or acceptor, the conductivity type of the grown layers were tested by the hot probe method. The photoluminescence experiments were done using a 0.5 m monochromator, a 100 mW Ar laser for excitation and lock-in techniques to filter the signal. The setup was controlled by a PC.

3. Results and discussion

The Sn-GaSb quasi-binary phase diagram has been previously determined and some experimental points have been reported at temperatures above 300 [5 - 9] and some works about thermodynamic properties of the ternary system have been reported.

| Table 1. Liquidus points of the Sn-Ga-Sb phase diagram. |
|---------------------------------------------------------|
| $T_{\text{Liq}}$, K | $X_{\text{Ga}}$ | $X_{\text{Sb}}$ | $X_{\text{Sn}}$ |
|-------------------|----------------|----------------|----------------|
| 508               | 0.01           | 0.01           | 0.98           |
| 520               | 0.013          | 0.013          | 0.974          |
| 534               | 0.015          | 0.015          | 0.97           |
| 546               | 0.018          | 0.018          | 0.964          |
| 552               | 0.796          | 0.001          | 0.203          |
| 557               | 0.02           | 0.02           | 0.96           |
| 564               | 0.023          | 0.023          | 0.954          |
| 566               | 0.99928        | 7.2E-4         | 0              |
| 566               | 0.997          | 7.0E-4         | 0.002          |
| 573               | 0.032          | 0.019          | 0.949          |
| 600               | 0.038          | 0.038          | 0.924          |
| 601               | 0.317          | 0.006          | 0.677          |
| 634               | 0.94           | 0.003          | 0.057          |
| 652               | 0.49           | 0.01           | 0.5            |
| 709               | 0.11           | 0.11           | 0.78           |

Table 1 shows the liquidus points measured in this work, when a layer was grown its conductivity type is indicated. The points corresponding to the quasi-binary part of the phase diagram are plotted in Fig. 1 together with some other points reported in the literature [5 - 9]. It can be seen that all points lie close to a continuous line. It is possible to estimate the heat of dissolution of GaSb in Sn using the approximation of ideal solutions by fitting the low temperature, low concentration data points to the equation:

$$X_{\text{GaSb}}^L = X_0 \exp(-\Delta H / RT)$$
The fitting gives a value of the heat of dissolution ($\Delta H$) of the order of 8.7 kcal/mol.

All the layers grown had P type conductivity, even those grown at temperatures lower than 400 C, at these temperatures GaSb layers grown from Ga solutions in a graphite boat normally exhibit N type conductivity [3]. This is indicative that Sn is incorporated into the GaSb layers as an acceptor impurity.

![Liquidus of the quasi-binary phase diagram Sn-GaSb.](image)

To confirm this observation an undoped GaSb layer was grown from a Ga solvent at 293 C and it had N type conductivity, as expected. Then other layers were grown at the same temperature but adding very small amounts of Sn to the liquid solution. It was observed that the conductivity of the layers changed to P type when the amount of Sn added was near 0.2 at. %.

The photoluminescence spectra of some of the grown samples from Ga solvent is shown in fig. 2.

![Photoluminescence spectra of layers grown from a Ga solvent doped with different amounts of Sn.](image)

Fig. 2. Photoluminescence of layers grown from a Ga solvent doped with different amounts of Sn.
The spectra of the sample grown with no added Sn shows two peaks, one at around 1530 nm can be attributed to near band gap transitions. The emission peak at lower energies is more intense, we have not searched for the origin of this peak. When 0.01 at. % of Sn is added to the liquid solution the near band gap peak disappears and a new peak at around 1590 nm appears in the spectrum and its intensity is still less than that of the lower energy peak, this new peak can be attributed to the Sn impurity as we will see. When the quantity of Sn is raised to 0.05 at. % the lower intensity peak disappears, the peak at 1590 nm is now the main feature of the spectrum and a smaller intensity peaks appears at around 1540 nm. Finally when the Sn content of the liquid solution reaches 0.2 at. % the emission shows only the peak at around 1590 nm. This behavior is in agreement with the assumption that the 1590 peak is due to transitions involving the Sn impurities.

4. Conclusions

Some points of the Sn-Ga-Sb phase diagram have been measured. Some of these points agree with previously reported data. GaSb layers have been grown using Sn as solvent at temperatures as low as 250 C. Sn incorporates into the grown layers as an acceptor impurity and so it cannot be considered as an “ideal neutral solvent” for the growth of GaSb. The photoluminescence spectra of these samples show a peak at around 1590 nm that can be attributed to the Sn impurities.

5. Acknowledgments

This work was partially supported by CONACYT, PROMEP and FAI at UASLP.

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