Materials Science Forum Vols. 196-201 (1995) pp. 1797-1800

STUDY OF GALLIUM AND ANTIMONY CLUSTER FORMATION IN GaSb BULK CRYSTALS GROWN FROM NONSTOICHIOMETRIC MELTS

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Keywords: Clusters, GaSb, Czochralski method, native acceptors.

Abstract. Bulk GaSb crystals have been grown by Czochralski method from nonstoichiometric melts. Formation of clusters and native acceptors as a function of the melt composition has been studied.

Introduction

One of the most promising directions in modern semiconductor research and technology is a creation of composite materials, where metallic or semimetallic particles are built in the semiconductor matrix. This approach was successfully realized on the base of GaAs grown by molecular beam epitaxy at low temperature [1,2]. This material exhibits several interesting properties due to formation of As precipitates in the high-quality crystalline GaAs matrix.

It seems to be of interest to extend the approach to different semiconductor materials and various growth techniques. We performed an attempt to form Ga and Sb clusters in GaSb bulk crystals grown by Czochralski method from nonstoichiometric melts.

On the other hand, nonstoichiometric growth conditions seem to be attractive as a method to control the concentration of so called "native" acceptors in GaSb. These acceptors are the major reason for p-type conduction of GaSb grown by various techniques. In the case of Czochralski-grown crystals the native acceptor concentration is as high as $(1\text{-}2)\cdot 10^{17}cm^{-3}$. The native acceptor is usually attributed to a Ga_{Sb} antisite defect. Its concentration was found to be strongly nonstoichiometry dependent when Ga-rich, Sb-rich and stoichiometric conditions were realized during liquid-phase epitaxy [3,4].

Experimental

The GaSb crystals were grown in [100] direction by Czochralski method in a hydrogen flow. A unified process was used for synthesis and crystal growth. The antimony concentration in the melt was varied from 48 to 53 at.%. To eliminate the twin formation, which often accompanies the growth of GaSb and other III-V compounds from nonstoichiometric melts, the growth rate was reduced to 0.2-0.5 mm/hour. The growth features have been discussed in more detail elsewhere [5]. The dislocation density in the crystals was about $5\cdot 10^{3}cm^{-3}$.

A Philips EM420 electron microscope operating at accelerating voltage of 100 or 120 kV was exploited in the study of structural perfectness of the crystals. The samples with [100] orientation were prepared for transmission electron microscopy (TEM) by mechanical dimple grinding and polishing and subsequent wet etching.

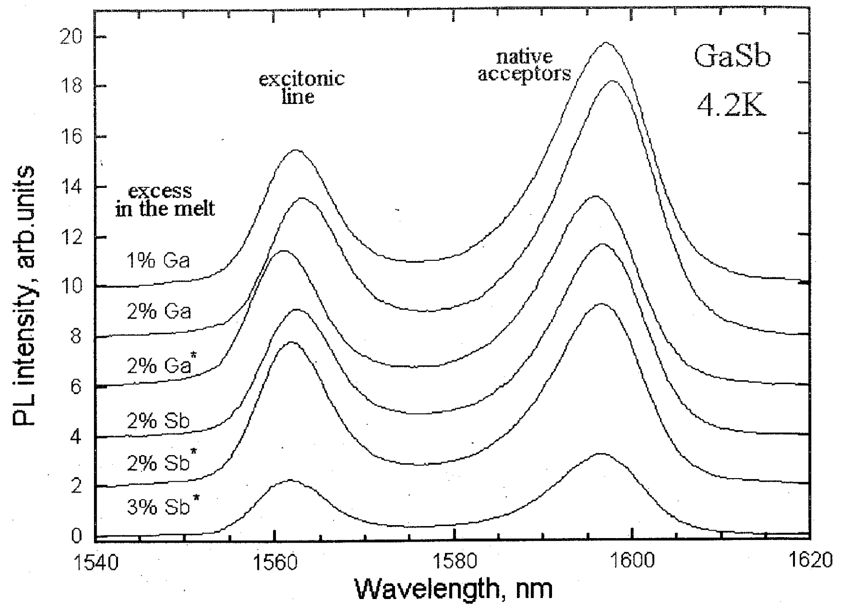


Fig.1. Photoluminescence spectra of the samples grown from the melts with different excess of Ga or Sb. (*) indicates the samples from the top of the crystals.

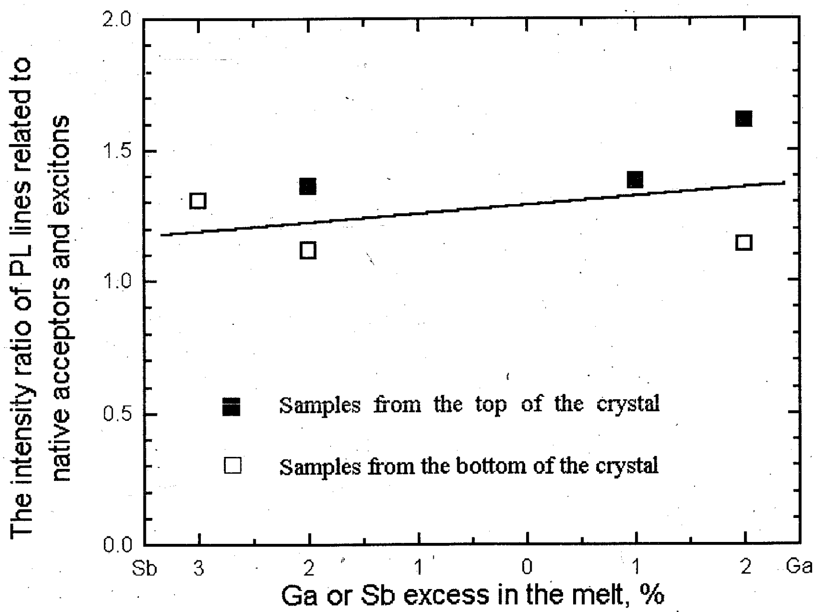


Fig.2. The intensity ratio of the PL lines indicates a weak increase in native acceptor concentration with Ga excess in the melt and more stronger one from the top to the bottom of the crystals.

The electrical parameters of the samples were measured at 77 and 300 K by Van-der-Pauw method. The measurements showed no pronounced dependence of the hole concentration and mobility on the melt composition. The hole concentration was ~$1 \cdot 10^{17} cm^{-3}$ at 300 K and (1-2)$\cdot 10^{16} cm^{-3}$ at 77 K. The hole mobility was 700 $cm^2/V \cdot s$ at 300 K and 3000 $cm^2/V \cdot s$ at 77 K. These values are typical of conventional Czochralski-grown GaSb.

The photoluminescence (PL) spectra were recorded at 4.2 K in the region of 1.54-1.80 μm using Ge-photodetector. A He-Ne laser with 1.13μm optical output of 3 mW and Ar^+-laser with 0.488μm optical output of 100 mW were used for PL excitation.

Results and Discussion

Fig.1 shows typical PL spectra recorded at high excitation density from the samples that were cut from top (starting) parts and bottom parts of the GaSb crystals grown from the melts with various Ga or Sb excess. Two major lines are characteristic of all the spectra. The line at lower energy (777 meV) relates to the radiative recombination of an electron with a hole captured by native acceptor. A slight variation in the energy position of this line for different samples seems to appear due to a variation in the shares of band-to-acceptor and donor-to-acceptor transitions.

The line at higher energy (795 meV) relates to excitonic recombination. When recorded under low excitation and at high resolution, the line has a non-symmetric and complicated form. This fact can be interpreted in terms of several different lines of bound excitons [3] strongly overlapped in our samples as a result of the high hole concentration. Presence of different elemental excitonic lines seems to be a reason for a slight variation in the excitonic band energy, when PL spectra are recorded from different samples under high excitation power (Fig.1).

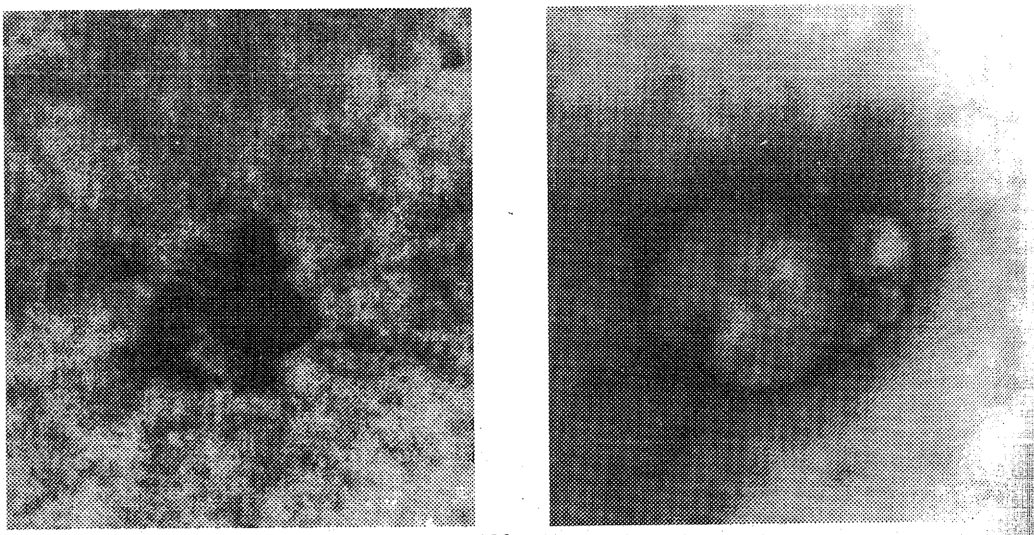
As can be seen from Fig.1, no drastic change takes place in PL spectra with nonstoichiometry variation in the melt. Fig.2 shows the intensity ratio of native-acceptor-related and excitonic lines as a function of Sb or Ga excess in the melt. Only a weak trend of this ratio can be noted. This fact evidences a weak influence of the initial melt composition on the native acceptor concentration.

A noticeable difference in the PL line ratio was detected for the samples cut from top and bottom parts of the same crystal. This effect was stronger in the case of Ga-rich melts and weaker in the case of Sb-rich melts. An antimony evaporation from the melt and low distribution coefficient of excessive gallium seem to be the major reasons for this phenomenon.

Therefore, use of Sb-rich melts is interesting in order to obtain bulk GaSb crystals with uniform distribution of the native acceptors.

The TEM study showed a low dislocation density and absence of twins in the GaSb crystals. No precipitates have been detected in the crystals grown from Sb-rich melts, at least when Sb excess was equal or less than 2 at.%. However, TEM revealed precipitates with the diameter of 100-300 nm and density of 10^9-$10^{10} cm^{-3}$ in the crystals grown from Ga-rich melts. Fig.3 shows these precipitates in a top part and in a bottom part of the crystal. The cluster size was found to increase with Ga excess in the melt. It should be mentioned that the cluster formation is not accompanied by generation of dislocations. The matrix around the clusters remains fairly perfect. This fact may be attributed to a low crystallization temperature and high plasticity of Ga.

So, we have shown that gallium clusters built in high-quality matrix can be obtained in the bulk GaSb grown from Ga-rich melts. However, the density of these clusters (10^9-$10^{10} cm^{-3}$) is much lower than that of arsenic clusters in GaAs grown by molecular beam epitaxy at low temperature ($10^{17} cm^{-3}$). Such a great difference in the cluster density seems to be due to dissimilar mechanisms of their formation. In the case of LTMBE-GaAs, when the growth temperature is as low as 200°C, excessive arsenic is incorporated into the crystal in a form of single or several atoms. The precipitation resulted from a decomposition of the supersaturated solid solution of As in GaAs matrix during subsequent annealing at high temperature of 600-700°C. In contrast, in Czochralski grown GaSb, when the temperature is as high as 710°C,



100 nm

a) b)

Fig.3. Bright-field TEM micrographs of Ga clusters in GaSb matrix. The samples were cut from a top part (a) and a bottom part (b) of the crystal grown from the melt with Ga excess of 2 at.%.

Ga clusters may be formed directly during the growth by a capture of small drops of the melt due to the high growth rate.

Summary

In conclusion, we have shown that perfect twin-free GaSb bulk crystals can be grown by Czochralski method from nonstoichiometric melts. The crystals with more uniform distribution of native acceptors along the growth direction have been obtained from Sb-rich melts. No precipitates have been revealed in these crystals. The use of Ga-rich melts leads to formation of gallium clusters. Their density is as high as 10^9-10^{10}cm^{-3}. The cluster size is 100-300 nm and depends on Ga excess in the melt.

Acknowledgments

The work is carried out under Russian National Programs: "Physics of Solid State Nanostructures" and "Fullerenes and Atomic Clusters". It has been supported by Russian Foundation of Fundamental Research (Grant No.95-02-05532).

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