



Effect of Er dopant in GaSb bulk crystals grown by vertical Bridgman technique

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Abstract

The distribution of Er in bulk GaSb ingots grown by vertical Bridgman technique has been investigated for different concentrations. The resistivity, mobility and carrier density were analysed. The formation of Er–Sb compounds and the incorporation of Er at subgrain boundaries has been shown by cathodoluminescence studies. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last years, rare-earth (RE)-doped III–V semiconductors have been extensively studied due to their ability to activate the emitting RE centres by minority carrier injection. In fact, there is an expectation for their possible applications as light-emitting devices in which RE would play an active role as the emission centres [1–3]. Moreover, in semiconductor-based lasers the rate

of peak wavelength shift with temperature influences the stability of the lasing wavelength which is an important characteristic to take into account in optical devices to be efficient light sources for coherent optical transmission systems [1,2]. In this way the presence of RE elements with sharp and temperature-independent luminescence could solve this situation.

It is well known that the 4f-shell transitions luminescence spectra of the RE ions show sharp lines even at high temperatures due to the screening effect of the outer-lying 5s² and 5p⁶ closed shells as has been reported for Er in InP, GaAs and InGaAs [3–9]. As a consequence RE ions in solid-state lasers can be optically excited by photons transparent to

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the host material. These properties are hoped to be of great advantage for the development of current-driven laser action in well-designed laser structures in contrast to the conventional semiconductor ones which work by means of broad temperature-dependent luminescence band-to-band transitions [1].

Moreover, in the field of the optical communications Er is a good choice for the development of RE semiconductor light emitting devices due to the intra-4f-shell transition corresponding to a wavelength of 1.54 μm which is the minimum of the absorption of silica-based fibers.

Furthermore other important features must be considered in order to understand the behaviour of RE in III–V semiconductor compounds: (i) the well-known tendency of the RE ions to form oxides due to their affinity to oxygen and to the VI group elements can be used to obtain a gettering effect of these elements acting as donors in III–V semiconductor compounds as reported for GaAs and InP [10,11], (ii) the formation of RE-group-V-element compounds known as pnictides and (iii) the 2 + charge state of the elements from the middle to the end of the RE group such as Er which may lead to the formation of acceptor states.

Vertical Bridgman (VB) technique has been extensively used for growing bulk GaSb crystals [12–14]. Unlike Czochralski crystal, VB-grown ones do not exhibit facets and impurity striations and possess better quality being adequate for their use as substrates for epitaxial growth [15].

In this work the effect of Er on the electronic properties in GaSb grown by VB has been studied for three different Er concentrations.

2. Experimental procedure

High-purity 99.9999% Ga, Sb and 99.9% Er metal were used as starting material to grow the Er-doped GaSb ingots with a doping level of 1×10^{19} at/cm^3 (ingot 25), 2×10^{19} at/cm^3 (ingot 26) and 8×10^{19} at/cm^3 (ingot 27), in high-quality quartz ampoules by VB method using an oscillating furnace which improves the homogenisation of the melt. The growth rate was 3 mm/h in a temperature gradient of about 35°C/cm. Details on this

technique can be found elsewhere [15]. The obtained ingots were 60 mm long and 12 mm in diameter. Several wafers were cut along the ingots with the surface perpendicular to the growth axis. They were mechanically polished with 5 and 1 μm alumina powder and chemically etched with a CP4 etchant ($\text{CH}_3\text{COOH} + \text{HF} + \text{HNO}_3 + \text{H}_2\text{O}$).

The Er concentration along the ingots 26 and 27 was determined by atomic absorption spectrophotometry (AAS) with a Perkin-Elmer 3110. High-quality AAS Er standards were used with a nitrous oxide-acetylene flame and a Perkin-Elmer Er hollow cathode lamp. The nature of the majority carriers, their concentration, mobility and resistivity were obtained in several samples by the van der Pauw technique with magnetic fields up to 7 kG and using indium dots as ohmic contacts which were previously verified. Finally cathodoluminescence (CL) analysis has been carried out in samples from the middle of the ingots using a Hitachi S-2500 SEM at 77 K and accelerating voltages of 25 kV by using a cooled Ge detector. Details of the CL experimental set-up are described elsewhere [16].

3. Results and discussion

The concentration profiles for the ingots 26 and 27 versus the solidified fraction are shown in Fig. 1. It can be observed that the concentration of Er is nearly constant during the first 70% of the length of the ingots. This behaviour is the same both at the centre and at the periphery for the two ingots. In the case of the ingot 26 the difference between the concentrations at the centre and at the periphery is higher than in the case of the ingot 27. This effect could be associated with a slightly more pronounced convective effect in the melt at lower concentrations. The last point at the end of each ingot shows an anomalous concentration due to the final transient state. If this last point is rejected the concentration profile can be well described by the Scheil law:

$$C_s(g) = K_{\text{eff}} C_0 (1 - g)^{K_{\text{eff}} - 1}, \quad (1)$$

being C_s the dopant concentration in the crystal, g the solidified fraction, C_0 the initial concentration

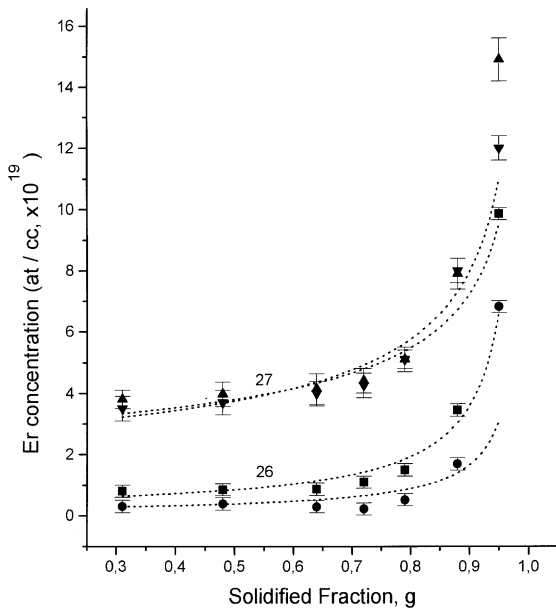


Fig. 1. Er concentration profiles at the centre (●) and at the periphery (■) for ingots 26 and 27. Dotted lines show the fit to the Scheil law given by Eq. (1).

in the melt and K_{eff} the effective segregation coefficient [17,18]. From the linearized expression [19]

$$\ln C = (K_{\text{eff}} - 1)\ln(1 - g) + \ln(K_{\text{eff}}C_0), \quad (2)$$

the values of the coefficient K_{eff} have been obtained for the two ingots 26 and 27 both at the centre and at the periphery which are shown in Table 1.

From this table one can conclude that at low concentrations the value of K_{eff} remains almost constant at the centre and at the periphery. For higher doping levels there is a noticeable difference between the value of K_{eff} at the centre and at the periphery due to the variations in the thickness of the solute boundary layer along the radial direction and to the sensitivity of the steady-state distribution coefficient K to high concentrations which produces certain variations on the value of K_{eff} [20]. Moreover, the difference between the values of K_{eff} for both ingots could be understood in the same way taking into account the dependence of the boundary layer thickness on the dopant concentration [20].

All the samples from the three ingots were analysed by van der Pauw technique showing a p-type

Table 1

Effective segregation coefficient for Er-doped GaSb

	K_{eff} (Centre)	K_{eff} (Periphery)
GaSb : Er (26)	0.09 ± 0.03	0.08 ± 0.02
GaSb : Er (27)	0.36 ± 0.03	0.44 ± 0.02

Table 2

Hall measurements for pure and Er-doped GaSb

	Resistivity (Ohms \times cm)	Density of holes ($\times 10^{17}$ cm $^{-3}$)	Mobility (cm 2 /V \times seg)
GaSb (Pure)	0.090	1.0	550
GaSb : Er (25)	0.035	5.0	330
GaSb : Er (26)	0.018	12	280
GaSb : Er (27)	0.0017	250	180

behaviour. Mean values of the resistivity, hole density and mobility are given in Table 2. These data show that the hole density increases with an increasing Er concentration. This effect is the responsible of the decreasing mobility and resistivity. However in a recent work from Sun et al. [21] the increasing concentration of Er in LPE GaSb layers grown on GaSb substrates, reduces the hole density. This disagreement could be understood by the presence of Er^{+2} in Er-doped GaSb bulk ingots which produces acceptor levels as has been pointed out for RE-doped III–V semiconductors [10]. Moreover one must consider that Sun et al. grew the layers on Te-doped GaSb substrates where the residual donor impurities, such as Te, could be reduced due to the high affinity for these donors by RE elements. In this way the formation of acceptor centres such as $\text{V}_{\text{Ga}}\text{--Te}_{\text{Sb}}$ could be suppressed [20].

In order to study the existence of Er–Sb precipitates, CL analysis has been carried out on samples taken from the central zone of each ingot. It has been found a high intensity level in the CL signal in these GaSb : Er samples. The CL images from sample 25 show a rather uniform intensity with dark subgrain boundaries (Fig. 2a). The appearance is similar to CL contrast observed in undoped GaSb samples [22] and precipitate-related features

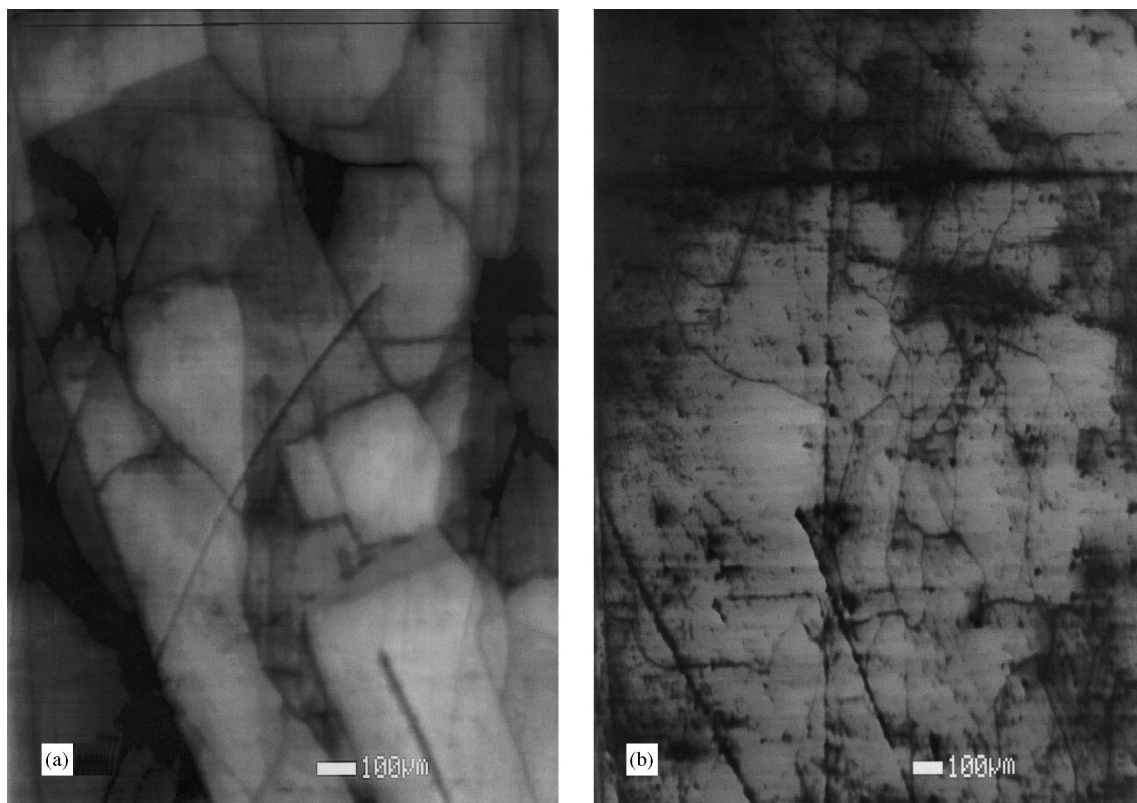


Fig. 2. CL Images for ingots (25) (a) and (26) (b).

have not been detected in this sample. By the contrary, dark regions between subgrains are probably due to the accumulation of Er in the subboundaries. For higher Er concentration, the CL image is shown in Fig. 2b. The structure of the grains is similar to that observed in Fig. 2a, but with smaller size of the grains. The CL images from the ingot 27 sample also reveal the subgrain structure. In the CL images of samples 26 and 27 dark precipitates of triangular shape equally oriented have been detected as shown in Fig. 3 probably due to the etching process. The density of these precipitates is larger in sample 27 than in sample 26. A chemical analysis carried out on the sample 27 inside and outside of the triangles is shown in Fig. 4. The incorporation of Er in precipitate-free region seems to be more homogeneous than in the sample 26 and the nature of the erbium precipitates could be Er_5Sb_3 compounds that crystallise in hexagonal phase [23] as can be concluded from our analysis. It must be

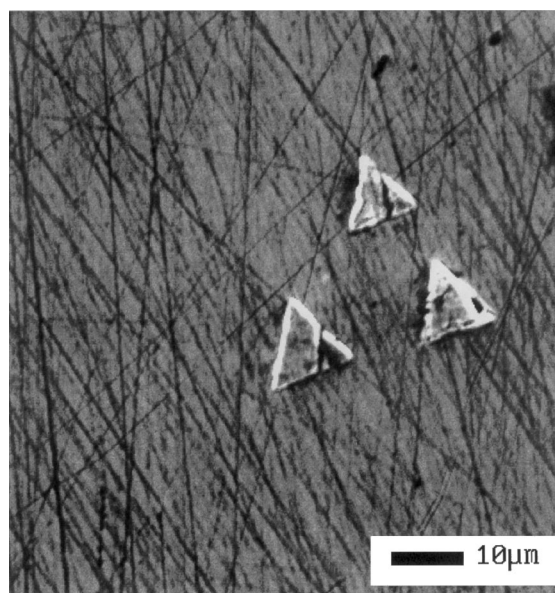


Fig. 3. Image from the precipitates present in ingot (27).

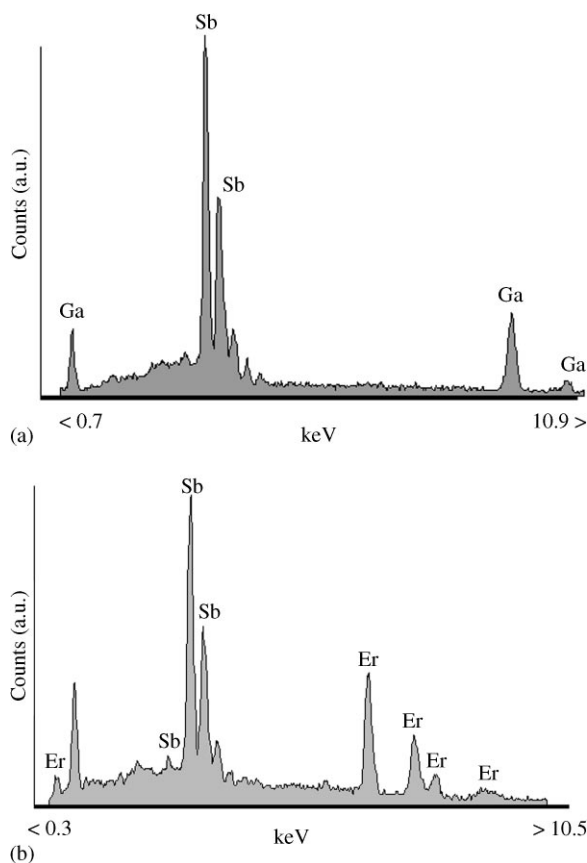


Fig. 4. EDAX analysis outside (a) and inside (b) of the triangles appearing in Fig. 3.

pointed out that from CL images one can observe that when the erbium concentration rises, the dislocation density also increases probably due to the formation of this precipitates which could introduce stresses in the lattice.

In conclusion in highly Er-doped bulk GaSb ingots, the hole concentration increases probably due to the acceptor levels created by the Er^{+2} ion. At the same time, the formation of the compound Er_5Sb_3 has been observed.

Acknowledgements

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