

# Cathodoluminescence Characterization of InGaSb Crystals

M.F. Chioncel, C. Díaz-Guerra, J. Piqueras, J. Vincent, V. Bermúdez and E. Diéguez

**Abstract** - The nature and the spatial distribution of radiative defects in  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  grown by the vertical Bridgman method have been studied by cathodoluminescence (CL) in a scanning electron microscope. The CL results have been complemented by X-ray microanalysis and backscattered electron imaging to relate the local luminescence properties to the chemical composition. Measurements of the band gap energy from the CL spectra, supported by X-ray compositional mappings, reveal an effective incorporation of In in the matrix, leading to the formation of the ternary alloy in the whole volume of the ingot. A band often observed in the CL spectra, peaked at about 20 meV below the band gap energy, is attributed to the presence in the ternary alloy of an acceptor level that would correspond to the  $V_{\text{Ga}}\text{-GaSb}$  acceptor in GaSb.

## I. INTRODUCTION

In the past decade, the III-V ternary alloy system GaSb-InSb has become of great interest for optoelectronic devices and high efficiency thermophotovoltaic (TPV) cells operating in conjunction with low-temperature radiators [1]. TPV cells with band-gaps lower than GaSb are expected to be advantageous for low-temperature (<1000 °C) non-wavelength selective TPV radiators because they provide more effective absorption of the black body infrared radiation [2]. This alloy covers an interesting low band gap range, (0.80 – 0.25) eV, that can be controlled by adjusting the In content to match the requirements. Strong efforts have been undertaken to grow compositionally uniform, crack-free materials. However, the growth of bulk good quality crystals remains an experimentally difficult task due to problems related to chemical segregation and mechanical stresses associated with the significant difference (12.5 %) between the tetrahedral radii of Ga and In [3]. The properties of the device employing  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  in the structure will ultimately depend on the material quality. In this work, the nature of luminescent centres and their spatial distribution along the growth and radial axis of an  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  ingot have been investigated using CL in the scanning electron

microscope (SEM). The information provided by CL was complemented by wavelength dispersive X-ray microanalysis (WDX) and backscattered electron (BSE) imaging.

## II. EXPERIMENTAL METHOD

The vertical Bridgman technique has been used to grow an  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  ingot, of about 12 mm diameter and a length of 40 mm, with a 10 % nominal In content. Several samples were cut at various places along the length of the ingot as shown in Fig.1. Three disks of 2 mm thickness were cut perpendicular to the growth axis and labelled D1, D2 and D3. Sample D1 corresponds to the bottom of the ingot, D2 to the middle part and D3 to the top of the crystal respectively. Samples L1 and L2, of rectangular shape, correspond to longitudinal sections (see Fig.1). This selection of the samples enables an efficient investigation of the distribution of the luminescent centres along both the growth and radial axis.

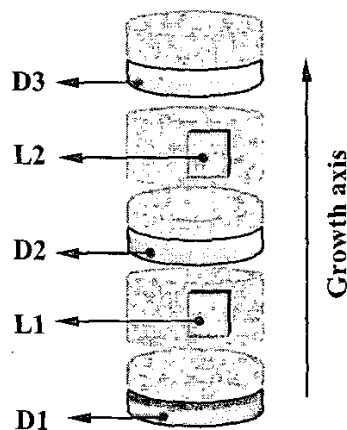


Fig 1. Scheme of the  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  ingot showing the positions and labels of the samples investigated.

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All the samples investigated were polished with alumina powder to a mirror finish and characterised by secondary electron (SE), BSE, WDX and CL modes of the SEM. Spatial and spectral CL measurements were carried out in a Hitachi S 2500 SEM with a cooled ADC

germanium detector. Measurements were performed at 90 K using a 20 kV accelerating voltage. CL spectra were recorded on each sample and deconvoluted using a sum of Gaussian line distributions in order to determine the different CL peaks contributing to the overall emission. The local In content has been determined from the position of the band-gap transition in the ternary alloy. In order to study the composition of the features observed in the CL micrographs and to understand the spectral distribution of the CL emission, mapping of the elements Ga, Sb, In as well as quantitative X-ray microanalysis were performed by WDX in a Jeol JXA-8900M Superprobe, using an accelerating voltage of 20 kV. The same system was used to obtain the BSE images.

### III. RESULTS AND DISCUSSION

Several representative areas were analysed by means of BSE and WDX. The X-ray compositional mappings show in all the samples a very uniform distribution of Sb and some anti-correlated variation in the Ga and In contents. There is a correspondence between contrast observed in CL, BSE, and X-ray mappings that is not observed in SE images, confirming that the mentioned contrast is not related to surface topography. Figure 2 shows the distribution of Ga and In and the corresponding CL and BSE micrographs of a selected area from sample D3. The lack of contrast in the Sb mapping (not shown) indicates a very uniform distribution of this element. Overall, our results indicate that a higher In content corresponds to a lower Ga concentration and that the Sb content is almost constant. CL panchromatic mappings of the investigated samples show similarities in the distribution of the radiative centres.

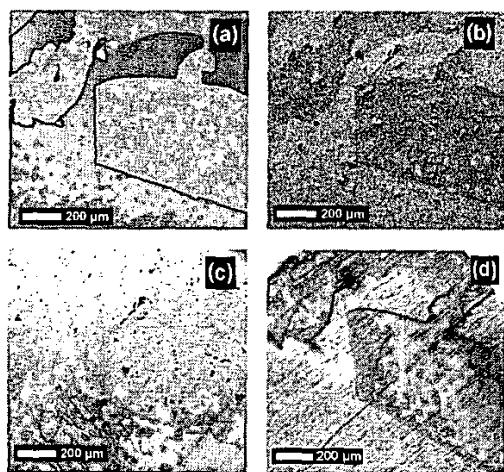


Figure 2. WDX mappings from sample D3 showing the In (a) and Ga (b) distribution. Darker greys correspond to a lower element content. (c) BSE image of the same area. (d) corresponding CL micrograph.

All the samples display luminescent emission, however with some areas of diminished or quenched CL emission. Actually, preferential agglomeration of areas of low CL emission can be observed in regions corresponding to the inner part of the ingot. Similar CL structures can be observed in all the samples investigated. Inside polygonal grains, high magnification micrographs of areas of enhanced CL emission show dark, precipitate-like defects and the absence of sub-grain boundaries. Some of the precipitate-like features appear randomly oriented, but most of them appear aligned in equally spaced parallel lines (Fig.3a). The size and the spatial distribution of these CL features, despite the precipitate-like appearance, suggest that they might be related to dislocations. Moreover, X-ray microanalysis of the regions where these dark features appear show no variation of In content. The attributed nature of these features to dislocations is also in agreement with previous results, which indicate that the solubility of In in GaSb is rather high and the formation of In precipitates unlikely [4], while strain-induced dislocations is one of the main problems found in the growth of good-quality  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  crystals [5]. The CL images of the areas of diminished CL emission show well-defined dark sub-grain boundaries (see Fig.3b).

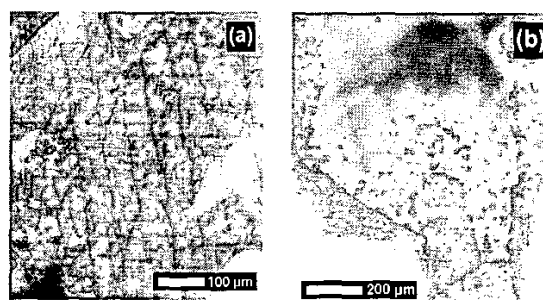


Fig. 3. CL images from sample D2 showing precipitate-like features aligned along parallel lines (a) and different polygonal grain structures and sub-boundaries (b).

Representative CL spectra of samples D1 and D3 are shown in Fig.4. A shift towards lower energies from the GaSb band gap value at 90 K, 796 meV, is clearly observed in all the spectra. This observation reveals the formation of the ternary alloy along the whole ingot. CL bands giving rise to these spectra have been determined from the best fits to the experimental data using a sum of Gaussian line distributions. The In content,  $x$ , has been calculated from the peak energy of the as-fitted band-gap emission [6]. Although some change of the peak position is observed in the spectra of a given sample, the mean band gap value over spectra recorded in the same sample could be considered as representative for the transversal sections of the ingot. The 760 meV band gap value characteristic for sample D1, corresponding to an In content of  $x=0.037$ , decreases to a mean value of 755 meV in sample D3, that

corresponds to an In content of  $x=0.042$ , while in sample D2 the mean band-gap value is almost the same than in sample D3. This gradient of the In composition of the ternary alloy is also clearly observed in the longitudinal sections (samples L1 and L2) when recording the spectral response along directions parallel to the growth axis.

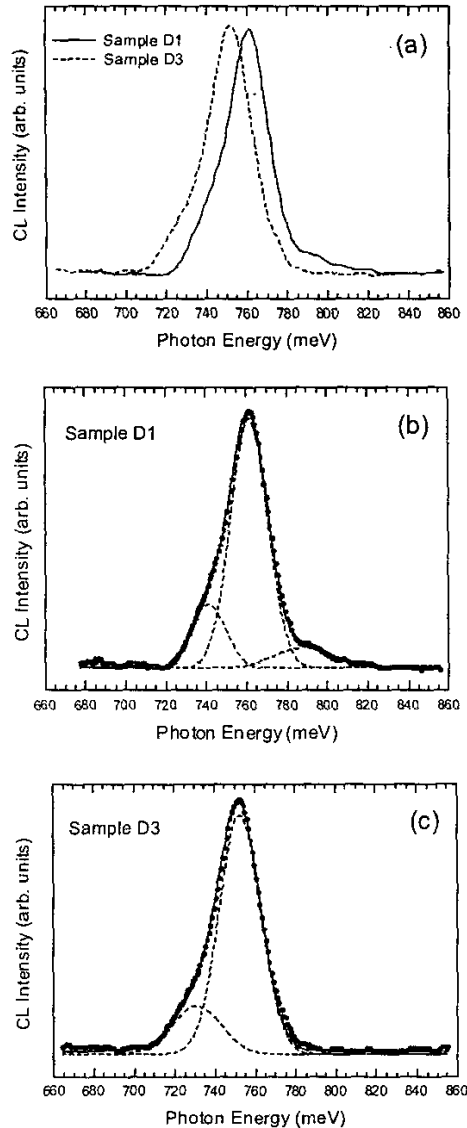


Fig. 4. (a) CL spectra representative of samples D1 and D3. (b) Gaussian deconvolution of the CL spectrum representative from sample D1. The emission bands appear centred at 761, 740 and 789 meV (dashed lines). The solid line is the best - fit curve while circles correspond to experimental data. (c) Deconvolution of the CL spectrum representative from sample D3. Emission bands are now centred at 752 and 731 meV.

Although the peak positions and the relative intensity of the emission bands may differ from spot to spot, deconvolution of our CL spectra always show two main transitions, one corresponding to the  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  band-gap emission and another one peaked at about 20 meV lower energy (Fig.4b, c). In some spectra a third weak emission, peaked at above band gap energies, is also observed.

Overall, the CL spectra of the ternary alloy exhibit similar qualitative features to those described for GaSb. It is well established [7] that as-grown undoped GaSb samples usually show at 90 K two main emissions peaked at about 796 meV (band-gap recombination) and 777 meV (commonly known as band A). The 777 meV emission is due to the transition from the conduction band to the neutral state of the native acceptor level  $V_{\text{Ga-GaSb}}$  [8]. The observed red-shift of the band edge luminescence in  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  is due to the reduction of the band gap energy with increasing  $x$ . A corresponding shift with In composition is observed for the lower and higher energy Gaussian peaks. A difference of about 20 meV between the  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  band gap emission and the lower energy peak was detected for all the spectra. Such band is probably related to the neutral state of a native acceptor level, equivalent to the acceptor responsible for the band A emission in GaSb. Some PL studies of  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  layers show only one transition which has been assigned to band-gap recombination [9], while Allegere et al. [10] conclude that a photoluminescence peak related to the acceptor level responsible for the p character of  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  becomes less intense with decreasing  $x$ . On the other hand, it was previously proposed [11] that In diffuses in GaSb by a vacancy mechanism on the Ga sublattice. Nevertheless, no comprehensive CL spectroscopic studies of defect bands in bulk  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  crystals have been previously carried out, mainly due to inefficient incorporation of In in the matrix. Furthermore, the only reported CL investigation of In-doped GaSb crystals [4] concluded that indium doping induces a certain reduction of the 777 meV band related to native defects, appropriate concentration of In leading to complete quenching of this luminescence band.

Our results suggest that  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  ternary alloy with  $x$  values ranging from approximately 0.035 to 0.055 exhibit qualitatively similar spectral emission as undoped GaSb. The dominant transition corresponds to the band-gap recombination in the ternary alloy. The lower energy emission appears to be related to a native acceptor of  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  similar to the native acceptor level  $V_{\text{Ga-GaSb}}$  of GaSb. The weak band centered above the band-gap transition energy observed in some spectra, can be associated to the corresponding higher energy transition observed in GaSb [7] related to tail states and shallow acceptors.

#### IV. CONCLUSIONS

The Bridgman method has been used to grow  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  ingots with good chemical homogeneity. CL spectral

measurements show a good incorporation of In in the matrix, leading to the formation of  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  ternary alloy along the whole ingot. Results provided by WDX and CL techniques also reveal the existence of a slight gradient of the In content along the growth axis. In addition, CL micrographs reveal the presence of grain boundaries and dislocations, while some cracks can be appreciated in SE and BSE images as well. These observations indicate that further work is still necessary in order to grow defect-free, single crystalline  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ . The CL spectra of the ternary alloy exhibit similar general features to those reported for GaSb. The red shift of the near band edge luminescence in  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$ , relative to that of GaSb, is due to the reduction of the band gap with increasing In content. Another CL band peaked at about 20 meV below the gap energy, is attributed to the presence in the ternary alloy of a native acceptor level that would correspond to the  $V_{\text{Ga}}\text{-GaSb}$  acceptor in GaSb.

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#### REFERENCES

- [1] P.S. Dutta, H.L. Bhat, and V. Kumar, "The physics and technology of gallium antimonide: an emerging optoelectronic material" 1997, *J. Appl. Phys.*, vol. 81, pp. 5821-5870.
- [2] O.V. Sulima, A. Bett, P.S. Dutta, M.G. Mauk, and R.L. Mueller, "GaSb-, InGaAsSb-, InGaSb-, InAsSbP- and Ge-TPV cells with diffused emitters", 2002, *29th IEEE Photovoltaic Specialists Conference*, New Orleans, pp. 892-895.
- [3] J.P. Garandet, T. Duffar, and J. Favier "Vertical gradient freeze growth of ternary GaSb-InSb crystals", 1990, *J. Cryst. Growth*, vol. 106, pp. 426-436.
- [4] P. Hidalgo, B. Méndez, J. Piqueras, P.S. Dutta, and E. Diéguez "Effect of In doping in GaSb crystals studied by cathodoluminescence" 1999, *Semicond. Sci. Technol.* vol. 14, pp. 901-904.
- [5] P.S. Dutta and A.G. Ostrogorsky, "Suppression of cracks in  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  crystals through forced convection in the melt", 1998, *J. Cryst. Growth* vol. 194, pp.1-7.
- [6] F.S. Juang, Y.K. Su, and T.S. Wu, "Relationship between solid and vapor phase compositions for  $\text{In}_x\text{Ga}_{1-x}\text{Sb}$  epilayers grown by MOCVD", 1991, *Solid State Electronics* vol. 34, pp. 1225-1229.
- [7] B. Méndez, P.S. Dutta, J. Piqueras, and E. Diéguez, "Cathodoluminescence studies of growth and process-induced defects in bulk gallium antimonide", 1995, *Appl. Phys. Lett.* vol. 67, pp. 2648-2650.
- [8] M.C. Wu and C.C. Chen, "Photoluminescence of high-quality GaSb grown from Ga- and Sb-rich solutions by liquid-phase epitaxy", 1992, *J. Appl. Phys.*, vol. 72, pp. 4275-4280.
- [9] J. Shin, Y. Hsu Y, T.C. Hsu, G.B. Stringfellow, and R. W. Gedridge, "InSb, GaSb, and GaInSb grown using trisdimethylaminoantimony", 1995, *J. Electron. Mater.* vol. 24, pp. 1563-1569.
- [10] J. Allegre, M. Averous, R. Jourdan, and A. Loullie, "Photoluminescence studies on  $\text{Ga}_{1-x}\text{In}_x\text{Sb}$  alloys", 1976, *J. Lumin.*, vol.11, 339-347.
- [11] D. Mathiot and G. Edelin, "Diffusion of indium in GaSb", 1980, *Phil. Mag. A*, vol.41, pp. 447-458.