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Cathodoluminescence microscopy of doped GaSb crystals

B. Méndez[a,*], J. Piqueras[a], P.S. Dutta[b], E. Dieguez[b]

[a]*Departamento de Física de Materiales, Facultad de Físicas, Universidad Complutense, E-28040 Madrid, Spain*
[b]*Departamento de Física de Materiales, Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain*

Abstract

We present the homogeneity and luminescence properties of bulk GaSb obtained by the cathodoluminescence (CL) technique in the scanning electron microscope. The samples used in this study are as-grown undoped and impurity diffused (tellurium) and doped (chromium) material. CL investigations have revealed a non uniform distribution of native defects in GaSb wafers. Post growth annealing in vacuum, gallium or antimony atmospheres causes an increase in homogeneity in CL images. Te diffusion and Cr doping provides new information about defects in GaSb. CL images and CL spectra recorded in these samples support that the type of defects formed is a function of diffusion time and impurity concentration.

Keywords: Cathodoluminescence; Diffusion time; Tellurium

1. Introduction

In recent years, gallium antimonide has generated interest as a potential substrate material for various lattice-matched devices operating in the range of about 0.3–1.6 eV. However, significant progress has to be made both in material characterization and processing before it can be widely employed for device applications. There are several reports on the growth of bulk GaSb single crystals [1–3] but little information is available regarding the characterization of defects in GaSb crystals. It is well known that the quality of epitaxial layers and the behaviour of devices made from them depend on the structural quality of the substrate. For this reason characterization of defects in bulk GaSb is a necessary step for the practical application of this material for micro and optoelectronic devices. The interest of defect studies refers to undoped and to crystals after doping with different electrically active impurities.

For defect characterization, cathodoluminescence (CL) in the scanning electron microscope (SEM) has been extensively applied to many semiconductors and semiconductor heterostructures. This technique which provides information on the nature and spatial distribution of the defects has been to our knowledge, only recently applied to characterize GaSb crystals as reported in previous works of our laboratory [4,5].

Undoped GaSb is p-type in nature with a high acceptor concentration. Acceptors are intrinsic and are due to gallium vacancies (V_{Ga}) and gallium antisites (Ga_{Sb}). We have investigated samples after annealing in vacuum, gallium and antimonide atmospheres to examine the evolution and nature of the native acceptors. Due to the presence of high concentration of acceptors impurity doping leads to compensation. In fact, controlled doping to low levels poses problems. One means of achieving that is dopant incorporation by impurity diffusion, which has been given limited attention to date. Te impurity can be used to obtain n-type material in a thin layer below the surface. In this paper we present results concerning the nature of luminescent centres after Te diffusion. During the course of this investigation on doped GaSb we have also carried out chromium doping. Chromium is known to create deep levels in III–V compounds like GaAs causing a semiinsulating behaviour. To our knowledge there are no reports on semiinsulating bulk GaSb. To see the possible effect of Cr doping on the native defect concentration, single crystals of GaSb:Cr were grown by the horizontal Bridgman technique and investigated by CL. In the present work, CL in the SEM is used to study the nature of defects in undoped as well as in Te and Cr doped samples.

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[*] Corresponding author.

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2. Experimental method

The samples used in this work were GaSb and GaSb:Cr single crystals grown by the vertical and horizontal Bridgman method. For the annealing treatments the wafers were prepared by conventional chemo-mechanical polishing. For the gallium annealing, 6 N pure gallium was spread on the wafer surface at room temperature. For annealing in antimony atmosphere, 6 N pure antimony balls were kept along with the wafer. Other wafers were annealed under a vacuum of 10^{-6} Torr. The annealing temperature and time was kept constant at 500°C and 12 h, respectively, for all the treatments. The Te-diffusion experiments were carried out in evacuated and sealed quartz ampoules at 500°C for 2, 15 and 24 h. Details of the diffusion experiments will be provided elsewhere [6].

For CL measurements a Hitachi S-2500 scanning electron microscope was used. Samples were at 77 K and the luminescence signal was detected with a North Coast EO-817 germanium detector.

3. Results and discussion

CL spectra of as-grown undoped samples (Fig. 1) show that two main emission bands peaked at about 796 and 775 meV, respectively, and a weaker emission at 756 meV. The 796 meV band corresponds to the band–band transition and the 775 meV, usually known as band A, has been attributed [7,8] to the presence of the acceptor level V_{Ga}–Ga_{Sb}. The band at 756 meV (designated as band B) has been related to a complex (V_{Ga}–Ga_{Sb}–V_{Ga}) arising from an excess of Ga vacancies [9], but its origin is not yet well determined. Annealing treatments provide some information on the possible origin of the luminescence bands (Fig. 2). For comparison, vacuum, Sb and Ga-annealed samples have been studied. CL spectra of annealed samples (Fig. 2(a)) reveal only the 775 and 756 meV bands. Fig. 2(b) shows CL spectra of the Ga annealed sample taken from two different positions in the sample, revealing that the intensity of the 756 meV transition enhances drastically (Fig. 2(b)). This result suggests that the band B is associated with a defect involving excess of gallium as a gallium antisite or related complex.

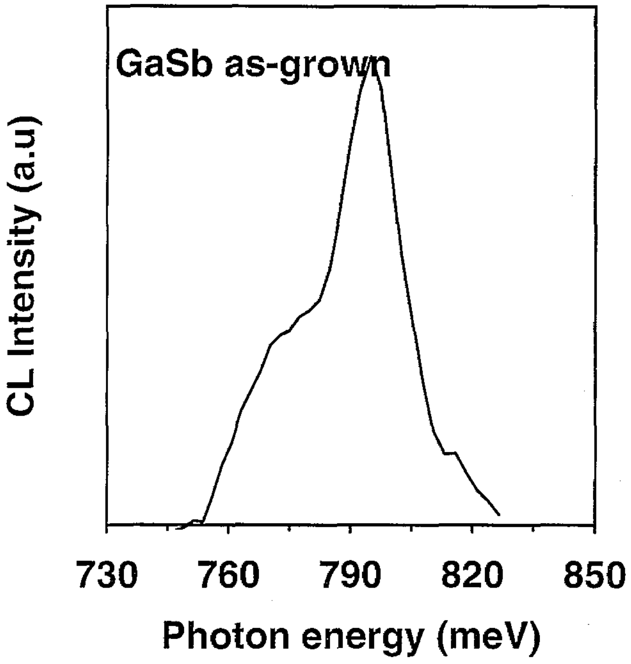

Fig. 1. CL spectrum at 77 K of a sample of as-grown undoped GaSb.

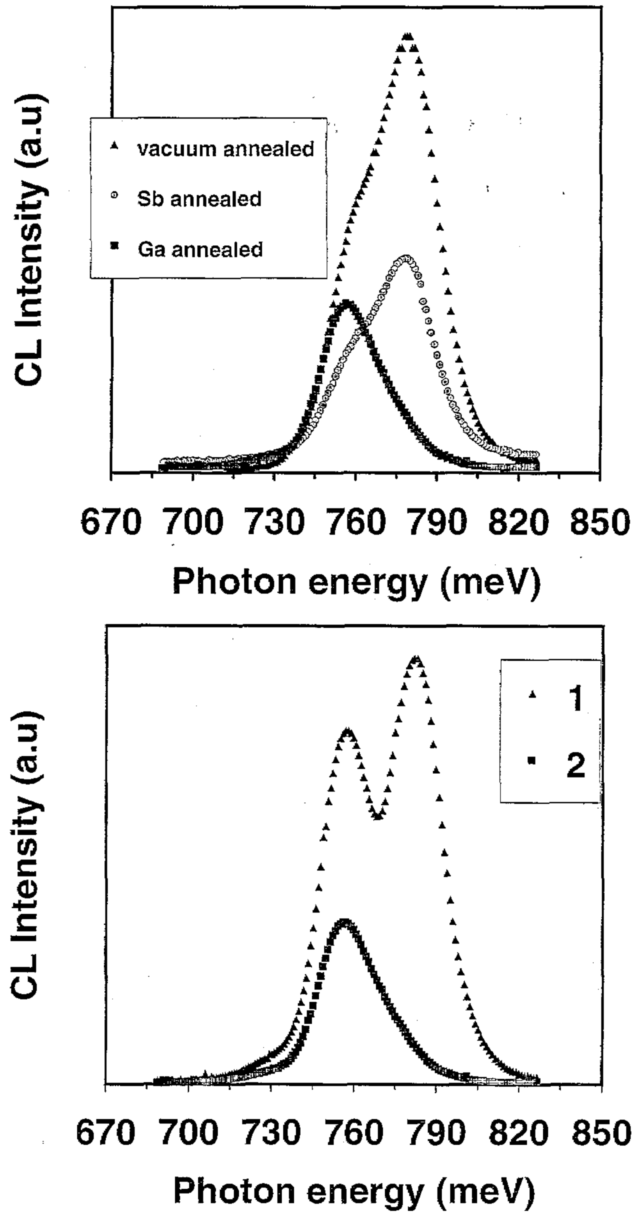

Fig. 2. CL spectra at 77 K of (a) vacuum, antimony and gallium annealed GaSb at 500°C, 12 h, and (b) CL spectra from gallium annealed obtained from different positions in the sample.

The CL images of as grown crystals show contrast related to subboundaries (Fig. 3(a)). Similar images are obtained in vacuum annealed samples but after annealing in Sb dark precipitate defects are observed (Fig. 3(b)). The Ga annealed sample shows a rather homogeneous distribution of CL intensity, which indicates the possibility of using Ga annealing treatments as a procedure leading to wafer homogeneity.

In Te-diffused samples the features observed in CL images are a function of the diffusion time. After short diffusion time (2 h) the contrast is similar to that of the undoped samples but show, as an additional feature, small dark dots probably due to decorated dislocations. Increasing annealing time leads to the formation of precipitate defects (Fig. 4) which could either be Te precipitates or the Ga_2Te_3 precipitates observed by transmission electron microscopy by other authors [10]. CL spectra of Te-diffused samples (Fig. 5) show a peak at 744 meV which has been attributed [11] to transition from conduction band to an acceptor state of the complex V_{Ga}–Ga_{Sb}–Te_{Sb}. The spatial distribution of this defect seems to be related to the presence of dislocations as CL images show. With an increase in Te concentration, the intensity of 744 meV peak increases (Fig. 5(a)), but in the sample with highest Te concentration, the 744 meV almost disappears while the 756 meV becomes the dominant transition (Fig. 5(b)). This effect can be explained by increasing volatization of Sb after long diffusion times. This results in Ga excess and the effect on CL spectra is similar to that caused by an excess described in the Ga-annealed undoped samples.

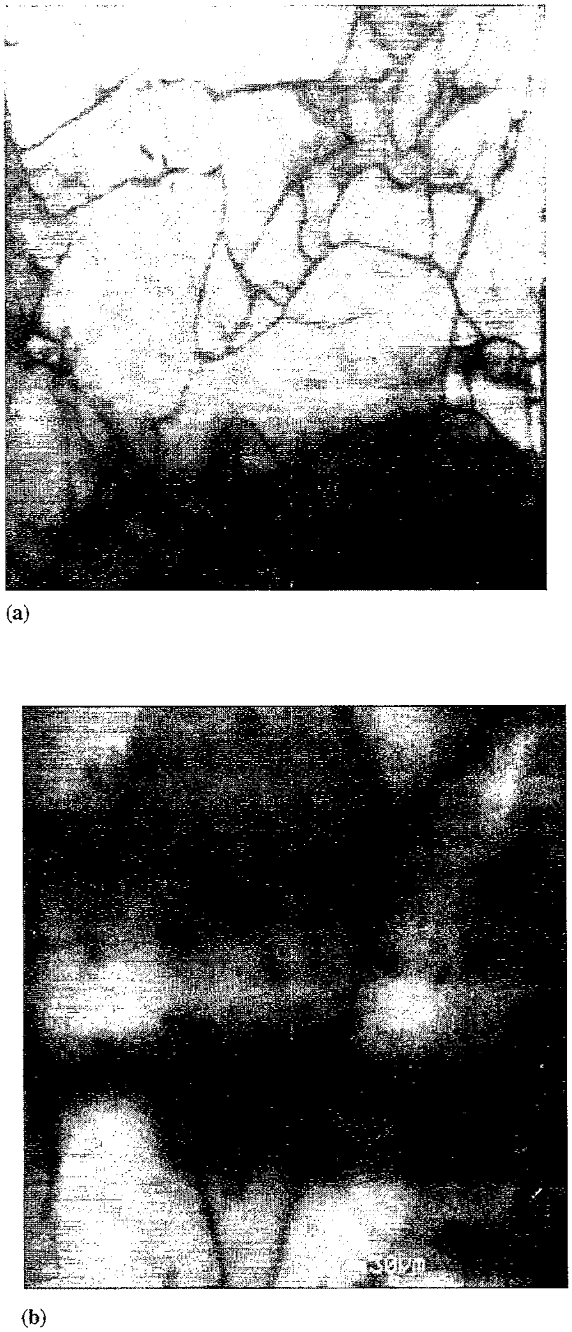

Fig. 3. CL images of (a) as-grown and (b) gallium annealed samples.

Fig. 4. CL image of Te-diffused GaSb (24 h).

The effect of Cr on the structure of luminescent centres, was studied on an ingot of approximately 20 mm length. CL spectra were recorded along the length and the influence of Cr concentration on the emission bands could be investigated. Even though there are no data, from electrical resistivity measurements, on the segregation coefficient of Cr in GaSb, we have observed that along the growth direction there is a segregation of Cr. Fig. 6 shows the CL spectra corresponding to Cr-rich and Cr-poor ends of the ingot. The spectra have been deconvoluted and the best fits obtained. In regions with a low concentration of Cr (Fig. 6(a)), a broad peak around 770 meV appears. This peak can be decomposed into two peaks at 778 and 770 meV of comparable intensity. In the opposite side of the ingot, the broad band corresponds to the 778 and 756 meV bands (Fig. 6(b)). In comparison with undoped crystals, all spectra obtained from the Cr doped ingot show a reduced intensity of band A which means that Cr doping decreases the concentration of the native acceptor responsible for this emission. The CL observations in GaSb:Cr can be explained by the formation of complexes involving Cr during the growth of the doped crystals. The formation of native defects in GaSb is believed to be initiated by the volatilization of Sb with the formation of Sb vacancies. This leads in a further step to the formation of Ga-antisites with the schema $Ga_{Ga} + V_{Sb} \rightarrow Ga_{Sb} + V_{Ga}$. In the presence of Cr, however, the complex $Cr-V_{Sb}$ is formed as observed in the case of GaSb:Mn by photoluminescence and electron spin resonance [12]. This results in an excess of Ga in the sample leading to an increase in the 756 meV band which, as described above, increases in Ga annealed samples.

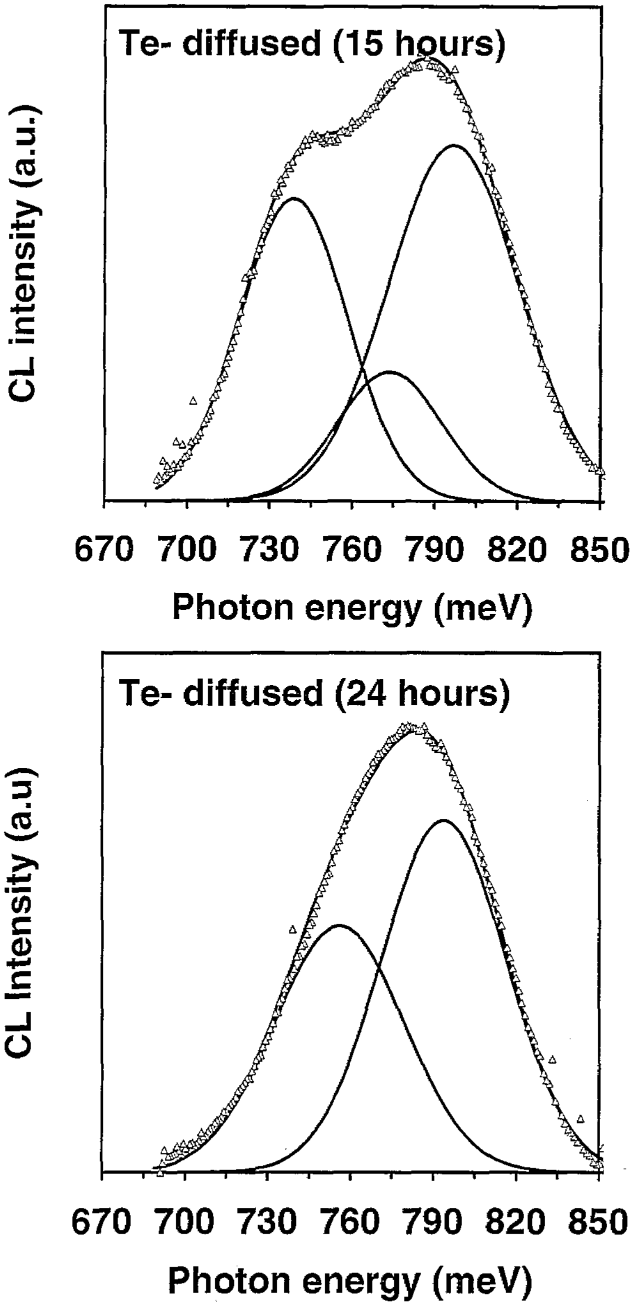

Fig. 5. CL spectra of Te-diffused samples (a) 15 h and (b) 24 h.

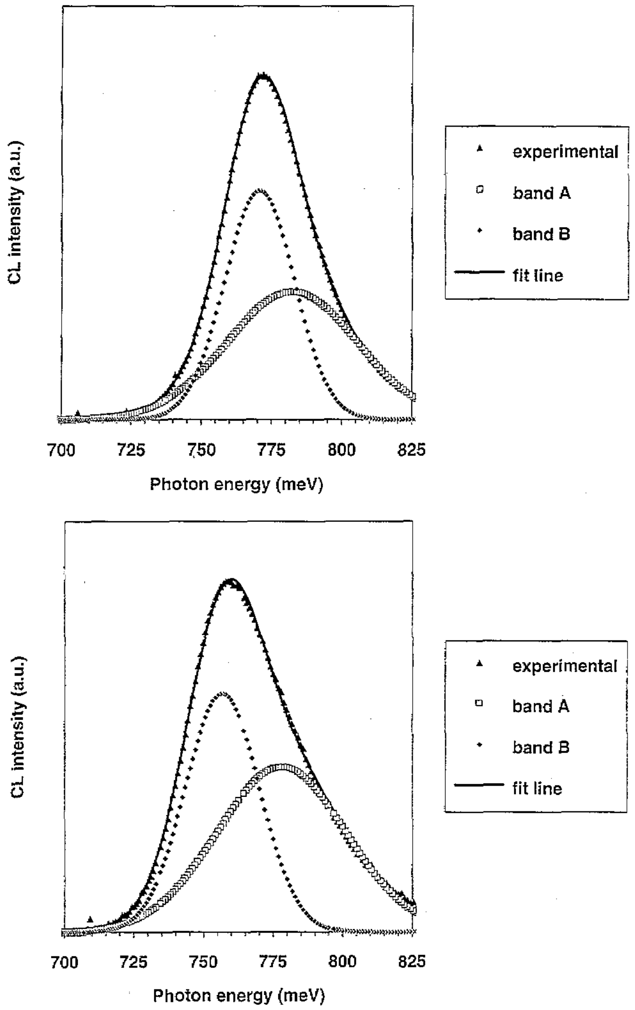

Fig. 6. CL spectra of Cr doped GaSb (a) low Cr and (b) high Cr concentration.

4. Conclusions

In conclusion, we have analyzed the nature and distribution of defects in GaSb by CL in the SEM through the evolution of luminescence bands. The samples investigated were as grown, Te diffused and Cr doped GaSb. The two main emission bands related to native defects are band A (777 meV) and band B (756 meV). The origin of the first one seems to be clear but the nature of centres that induce band B remains unknown. In a previous work made on annealed undoped samples we have suggested that Ga atoms are involved in the center responsible for the B emission. In this work, we have obtained new results concerning the origin of band B when we study Te diffuse and Cr doped samples. The results confirm the assumption that an excess of Gallium enhances the 756 meV emission.

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