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Cathodoluminescence study of the radiative recombination properties of Se-doped GaSb crystals

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The radiative recombination properties of Se-doped GaSb crystals grown by the Bridgman method have been investigated by cathodoluminescence (CL) microscopy and spectroscopy in the scanning electron microscope. A CL band centered at about 765 meV, not previously observed in undoped GaSb, is generally the dominant emission. CL spectra recorded under different excitation conditions suggest that this band can be attributed to a Se-related level–to–band transition. The spatial distribution of the 765 meV emission, as observed in the CL images, indicates an inhomogeneous Se distribution in the material. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1834727]

I. INTRODUCTION

Gallium antimonide is one of the most interesting III-V semiconductors from a technological point of view due to its applications in high speed electronics and long wavelength optoelectronic devices, like midinfrared lasers, photodiodes, infrared detectors, and thermophotovoltaic cells.[1–3] Actually, GaSb can be lattice matched with ternary and quaternary III-V alloys for fabrication of optoelectronic devices operating in the (0.8–4.1) μm range.[1] One of the basic units of optoelectronic devices on GaSb are *p-n* junctions. Undoped GaSb is almost always *p*-type irrespective of growth techniques and conditions. The residual native acceptor is related to a Sb deficiency and is generally considered to be due to the $V_{Ga}Ga_{Sb}$ defect.[1,4,5] On the other hand, *n*-type conduction in GaSb has been mainly achieved by Te, Se, or S doping.[6,7] The optimization of minority-carrier devices, including photovoltaic devices, strongly depends on various recombination processes such as recombination at surfaces and interfaces, Auger recombination, and especially in III-V compounds, radiative recombination. An understanding of these processes is critical to the improvement of materials and for the design of antimonide-based thermophotovoltaic (TPV) devices.[8,9] Among the *n*-type dopants, Te has been mostly used, while sulfur doping is more difficult due to its high evaporation rate.[1] Te doping frequently leads to the formation of deep acceptor states, like the antisite complex $V_{Ga}Ga_{Sb}Te_{Sb}$. Previous cathodoluminescence (CL) and photoluminescence studies[10–12] of this semiconductor reported emission bands in the 720–740 meV spectral range corresponding to radiative transitions involving Te-related acceptors. On the contrary, the influence of Se doping on the CL properties of GaSb crystals has not been investigated. In the present work, the radiative recombination properties of Se-doped GaSb crystals grown by the Bridgman method have been investigated by CL microscopy and spectroscopy in a scanning electron microscope (SEM). The nature and spatial distribution of the defects giving rise to the observed emission was found to depend on the region of the crystal examined. Furthermore, the obtained results revealed significant differences between the CL spectral distribution of the Se-doped samples and that previously reported for the Te-doped material.

II. EXPERIMENT

Se-doped GaSb ingots were grown by the vertical Bridgman technique without seeding. Ampoules containing 25 g of 6 N starting powder material, with nominal Se concentration of 2×10^{19} cm^{-3}, not previously graphitized, were evacuated up to 10^{-5} Torr and sealed. Powder material in the ampoule was melted at 950 °C during 24 h. The melted material was homogenized by low shaking the furnace for 30 h (+/−30° rotation around the horizontal position at 60°/h). The solidification pulling rate was set at 3 mm/h in a temperature gradient of about 40 °C/cm. After solidification, the furnace was slowly cooled down to room temperature. Hall measurements indicate a free-carrier concentration of n$\sim1\times10^{19}$ cm^{-3}.

CL investigations were carried out in a Hitachi S-2500 SEM with a cooled ADC germanium detector. Measurements were performed in a disk-shaped sample cut from the middle

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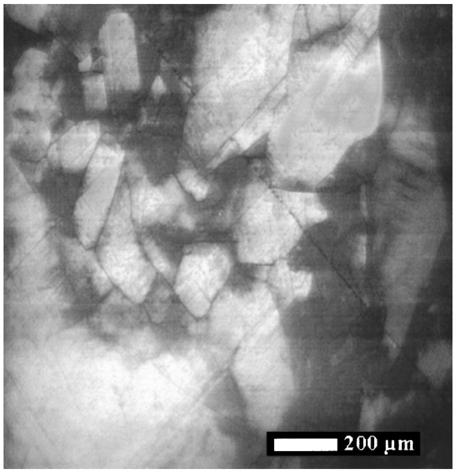

FIG. 1. CL image from the rim of the crystal revealing the grain structure of the investigated material (T=87 K).

of an ingot, at temperatures between 87 and 200 K, using a 20 kV accelerating voltage. The recorded CL spectra were deconvoluted using a sum of Gaussian line distributions in order to determine the different bands contributing to the emission. Wavelength dispersive x-ray microanalysis (WDX) were carried out in a Jeol JXA-8900M Superprobe to study the composition of certain features observed in CL micrographs.

III. RESULTS AND DISCUSSION

CL emission was mapped along several diameters of the sample in order to investigate the spatial distribution of the luminescent centers and to reveal the presence of different kinds of defects. A well-defined grain structure is clearly visible in the CL micrographs from the rim of the crystal (Fig. 1). The grain size varies between 100 μm and 1 mm approximately. These images show reduced radiative recombination efficiency at the grain boundaries and inhomogeneous spatial distribution of luminescence. In fact, clear differences between the CL intensity of different grains can be appreciated. On the contrary, CL micrographs of the center of the sample usually reveal a drastic increase of the grain size and a more uniform and intense CL emission. In certain regions, located at an intermediate position between the rim and the center of the sample, a cell-like structure is observed [Fig. 2(a)]. Curved boundaries separate areas of reduced CL intensity from cells containing dark spots on a bright background [Fig. 2(b)]. CL images from the center of the crystal reveal dark spots about 5 μm in size, usually surrounded by bright halos (Fig. 3). WDX measurements indicate that these spots do not correspond to Se-rich precipitates. The dot-and-halo contrast observed in Figs. 2 and 3 has been previously observed in CL images of a number of semiconductors, including Se-doped GaAs and Te-doped GaSb, and attributed to dopant segregation around dislocations.[13,14]

The spectral distribution of the CL emission at 87 K is shown in Fig. 4. CL spectra recorded under high excitation density conditions appear peaked between 780 and 785 meV, depending on the position on the sample considered. Gaussian deconvolution reveals the existence of two main emission bands centered at about 794 and 765 meV. A weak band centered near 830 meV, attributed to a transition involving tail states and shallow acceptors,[15] is sometimes observed. When the SEM electron beam is defocused the excitation density is reduced. Actually, in the experimental setup used in the present work the current density is reduced almost two

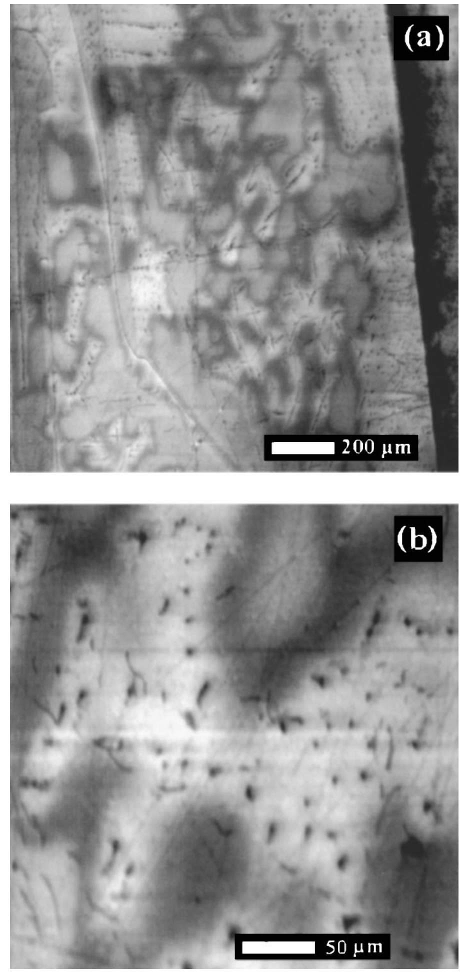

FIG. 2. CL micrographs from the Se-doped GaSb crystal revealing cell-like structures (a) and dark spots corresponding to dislocations inside one of the cells (b).

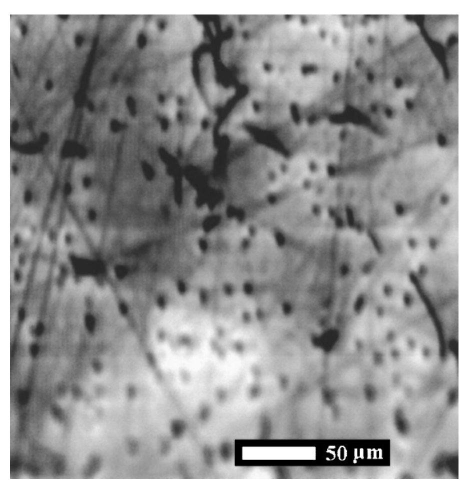

FIG. 3. CL image from the center of the crystal showing both dark dot dislocation contrast and dot and halo contrast.

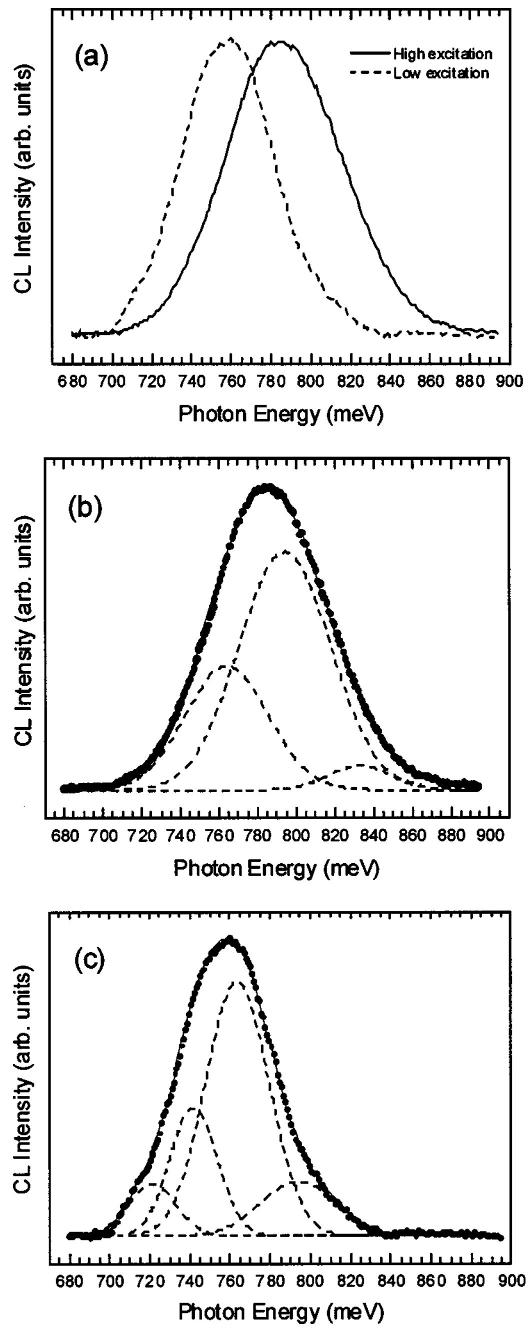

FIG. 4. (a) Normalized CL spectra from the GaSb:Se crystal recorded under high and low excitation conditions. (b) Gaussian deconvolution of the CL spectrum recorded under high excitation density reveals three bands centered at 794, 765, and 832 meV (dashed). (c) Deconvolution of the spectrum recorded under low excitation density shows four bands centered at 795, 765, 742 and 721 meV (dashed). Solid lines represent best-fit curves while circles correspond to experimental data.

orders of magnitude by defocusing the SEM electron beam. As a consequence of the presence of radiative centers with a low concentration, the intensity of the CL bands related to deep levels increases[16] and the shape of the spectrum changes. In fact, spectra from Se-doped GaSb recorded in such conditions appear centered between 755 and 765 meV [Fig. 4(a)]. Gaussian deconvolution reveals the existence of four bands centered at 795, 765, 741, and 720 meV [Fig. 4(c)]. The parameters of the Gaussian components determined from CL spectra of the investigated material are summarized in Table I. The band peaked at 765 meV is always the dominant emission, while the intensity of the 741 meV CL band is higher near the rim of the crystal and decreases towards the center. The band centered near 720 meV is usually weak and quenches at about 130 K. Kosicki and Paul[17] observed PL at 716 meV in Se-doped GaSb at 77 K although reported no spectral analysis of the emission, which was attributed to a donor-acceptor pair transition. The 795 meV band corresponds to the GaSb band edge transition, while the 765 meV band has not been previously observed in undoped GaSb. Deep level transient spectroscopy measurements indicate the existence of a deep level located at about 140 meV from the conduction band in Bridgman-grown GaSb:Se crystals,[18] but information concerning shallow states introduced in the direct band gap by the Se dopant is lacking. We tentatively attribute the 765 meV CL emission band to a Se-related defect level. Indeed, spectra recorded in the bright haloes surrounding dislocations (Fig. 2), show a dominant 765 meV emission and are almost identical to those recorded in more extended areas under low excitation conditions [Fig. 4(b)]. Hence, our results evidence a nonhomogeneous Se distribution in the sample. Actually, a higher dopant concentration influences the dislocation CL contrast, giving rise to the bright haloes observed around the dark dislocation dots,[19,20] as generally observed in the area imaged in Fig. 3. Moreover, different defect patterns and Se segregation coefficients have been observed in the central core and noncore regions of Se-doped GaSb crystals by previous transmission electron microscopy (TEM) investigations.[21] This inhomogeneous Se distribution may lead to nonuniform electrical transport in the material, which is undesirable for applications of doped GaSb in optoelectronic devices. Deconvolution of CL spectra recorded as a function of temperature (not shown) reveals that the 765 meV band is centered at about 762 meV at 170 K. Furthermore, the position of this peak is almost independent of the excitation density (Fig. 4). These observations suggest that the 765 meV emission is not related to a donor–acceptor pair transition but rather to a level–to–band transition. Although further work is needed to establish the donor or acceptor character of this level, it should be mentioned that the 765 meV CL band shares certain similarities with the intense CL band centered at 740 meV observed in Te-doped GaSb. Such emission is attributed to $V_{Ga}Ga_{Sb}Te_{Sb}$ acceptors, and the spatial distribution of this complex seems to be connected to dislocations.[10] In our Se-doped crystal, an enhanced 765 meV emission is also observed near dislocations,

TABLE I. The peak positions (E_p), full widths at half maximum (FWHM) and normalized intensities of the Gaussian components [see Figs. 4(b) and 4(c)] determined from CL spectra of Se-doped GaSb (T=87 K).

Excitation conditions	E_p (meV)	FWHM (meV)	Normalized intensity
High current density	794±2	51±3	1
	765±2	42±4	0.5–0.6
	830±3	39±3	0.1
Low current density	795±2	48±3	0.2–0.3
	763±3	39±4	1
	741±2	28±3	0.4–0.5
	720±3	26±3	0.2

while previous TEM investigations of this material[21] support the formation of donor-vacancy Se_{Sb}-V_{Ga} complexes. Thus, a defect similar to that responsible for the 740 meV band in Te-doped GaSb may be involved in the 765 meV band observed in the Se-doped crystals here investigated.

IV. CONCLUSIONS

In summary, the radiative recombination properties of Se-doped GaSb crystals have been investigated by CL microscopy and spectroscopy. CL micrographs evidence a nonhomogeneous Se concentration in the sample that strongly influences the luminescence spatial distribution. In particular, cell-like structures as well as dot-and-halo contrast related to dopant segregation around dislocations has been observed. A strong luminescence emission centered at 87 K at about 765 meV, not previously observed in undoped GaSb, is revealed by CL spectroscopy. This band is attributed to a Se-related level–to–band transition.

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