

Nature of compensating luminescence centers in Te-diffused and -doped GaSb

P. S. Dutta

Department of Physics, Indian Institute of Science, Bangalore-560 012, India

B. Méndez and J. Piqueras

Departamento de Física de Materiales, Facultad de Físicas, Universidad Complutense, E-28040 Madrid, Spain

E. Dieguez^{a)}

Departamento de Física de Materiales, Universidad Autónoma, Cantoblanco, 28049 Madrid, Spain

H. L. Bhat

Department of Physics, Indian Institute of Science, Bangalore-560 012, India

(Received 17 July 1995; accepted for publication 16 April 1996)

Diffusion of tellurium in undoped *p*-GaSb has been carried out. Using the cathodoluminescence and photoluminescence techniques, the luminescence centers in Te-diffused samples have been identified and compared with the Te-doped bulk GaSb. Fundamental differences in the radiative levels are observed between the diffused and the as-grown doped samples. Evidence for self-compensating acceptor complexes are seen in diffused samples. With short and moderate diffusion times, a compensating acceptor complex $V_{\text{Ga}}\text{Ga}_{\text{Sb}}\text{Te}_{\text{Sb}}$ is observed. For long diffusion times, the dominant acceptor center has been attributed to the antisite defect Ga_{Sb} or related complex. The reasons for the formation of various acceptor centers have been discussed. © 1996 American Institute of Physics. [S0021-8979(96)07014-4]

I. INTRODUCTION

In recent years gallium antimonide has generated a lot of interest by virtue of it being a potential substrate material for devices in the band-gap range of 0.3–1.58 eV.¹ At present, GaSb technology is in its infancy and significant progress has to be made both in materials and processing aspects before it can be employed for device applications. Due to the presence of high concentration of native acceptors, impurity doping to obtain *n*-GaSb always leads to compensation.^{2,3} As a result, the mobility of electrons reduces and controlled doping to very low levels poses problems. Dopant incorporation by diffusion has been given limited attention until now.¹ Such a study assumes all the more importance for basic *p*-*n*-junction device structures such as light-emitting diodes (LEDs) and photodetectors. This article presents a comprehensive treatment of the nature of luminescence centers in Te-diffused GaSb. Comparative study with Te-doped bulk GaSb single crystals with similar doping levels is also made.

II. EXPERIMENTAL DETAILS

Vertical Bridgman-grown single crystals of undoped *p*-GaSb were used for our studies.⁴ For the diffusion experiments, undoped *p*-GaSb crystals grown from stoichiometric melts were used. The net acceptor concentration of the undoped samples was approximately 10^{17} cm^{-3} . Te diffusion was carried out in evacuated and sealed quartz ampoules at 500 °C for 2, 15, and 24 h. Prior to diffusion, the quartz ampoules were prebaked at 800 °C under 10^{-6} T to remove any volatile contaminants. The volume of sealed ampoules

was about 6 cm^3 . The diffusion source mass amount was approximately 100 mg. During the diffusion experiments, the wafers of GaSb were placed along with Te. Pieces of Sb were also kept to create an overpressure of Sb during the diffusion cycle. Diffusion was simultaneously carried out on several samples under identical conditions. At the end of diffusion, the ampoule was withdrawn from the furnace and cooled rapidly in liquid nitrogen to condense the Te vapor on the ampoule wall and thus prevent any metallic condensation on the sample surface. The wafers were rinsed in organic solvents and HCl before any measurements. No visible degradation of the sample surfaces occurred even after 24 h of heat treatment. The depth profiles of the net donor concentration of various samples were evaluated from the capacitance–voltage (*C*–*V*) measurements at room temperature. The back ohmic contacts were provided by alloying indium and the Schottky contacts by evaporating gold dots of 0.4 mm in diameter. The homogeneity and luminescence properties of the Te-diffused samples have been studied by the cathodoluminescence (CL) technique. The CL measurements were carried out using a Hitachi S-2500 scanning electron microscope in the emissive and CL modes at 77 K. A liquid-nitrogen-cooled North Coast EO-817 germanium detector was used for the signal detection. The details of experimental setup for spectral and panchromatic CL measurements are presented elsewhere.⁵ To investigate the luminescent centers in Te-doped bulk crystals, photoluminescence (PL) measurements were carried out using MIDAC Fourier transform PL spectrometer.⁶ An argon-ion laser operating at 5145 Å was used as the excitation source with excitation level of 166 mW/cm^2 . Liquid-nitrogen-cooled germanium photodetector was employed for signal detection. A

^{a)}Author to whom correspondence should be addressed.

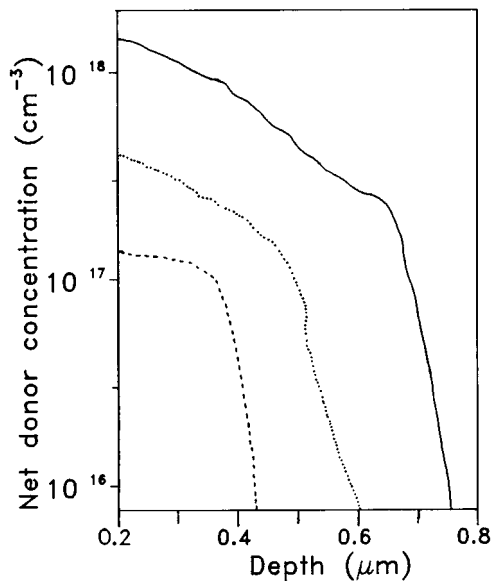


FIG. 1. Depth profiles of net donor concentration in Te-diffused samples. Diffusion times are 2 (dashed line), 15 (dotted line), and 24 h (continuous line).

resolution of 0.5 meV was used in our measurements. All PL spectra were recorded at 4.2 K by freely suspending the samples in liquid helium.

III. RESULTS AND DISCUSSION

Typical depth profiles of the net donor concentration in the diffused samples as evaluated from the $C-V$ characteristics are shown in Fig. 1. Several samples from the same batch were investigated. The depth profiles were found to be identical for all the samples diffused for the same time. The overall doping concentration and depth of diffusion increase with increase in diffusion time. CL measurements have been performed at an acceleration voltage of 20 kV. With this energy the penetration depth of the electron beam is almost 1 μm . Thus, the information we obtain is an average over the Te-diffused region. At lower acceleration voltages, the luminescence efficiency is not high enough to obtain accurate CL spectra. Figure 2 shows the CL images of the Te-diffused samples. The sample for which the diffusion was carried out for 2 h appeared to be almost precipitate free [see Fig. 2(a)], but small dark dots of 1–2 μm size are clearly revealed. This contrast could be due to the decoration of dislocations associated with the presence of tellurium as in other III–V compounds.⁵ In undoped GaSb, CL images show dark contrast related to the presence of subboundaries in the material and the inner portion of the grains appears uniformly bright.⁷ With increase in diffusion time to 15 h, precipitates start appearing throughout the sample. The size and concentration of the precipitates increase with further increase in diffusion time. For the sample with 24 h of diffusion, large clusters and precipitates could be seen [Fig. 2(b)]. Characterization of extended defects in heavily Te-doped Czochralski-grown GaSb single crystals has been carried out by Doerschel and Geissler.⁸ The nature and density of the defects are correlated with the local Te concentration. Prismatic dislocation

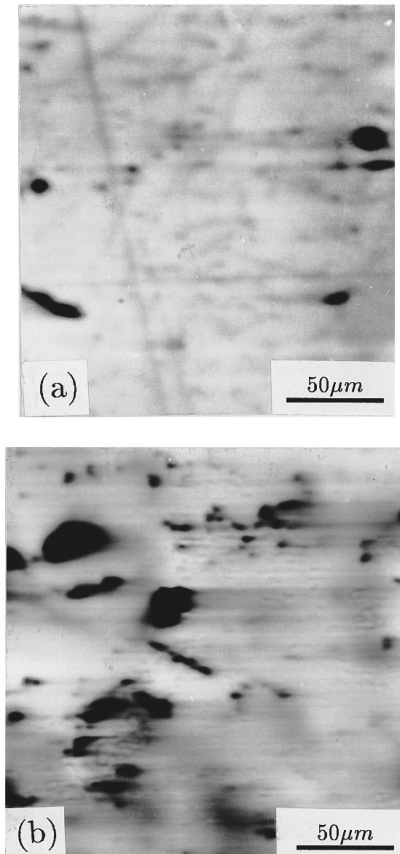


FIG. 2. Cathodoluminescence images of GaSb diffused with Te for (a) 2 h and (b) 24 h.

loops are generated at Te concentration of about $3 \times 10^{18} \text{ cm}^{-3}$ and dislocation clusters and large planar defects occurs at Te concentration of about 10^{19} cm^{-3} , which is close to the solubility limit of Te in GaSb. The planar defects have been identified as Ga_2Te_3 precipitates.⁸ In our case, the precipitates can be either due to Te or Ga_2Te_3 . This point is elaborated below while discussing the CL spectra of the samples.

The CL spectra of the diffused samples are shown in Fig. 3. Different regions of the same samples exhibit reproducible CL spectra in all studied cases. The energy positions and the full width at half-maximum (FWHM) of each peak have been determined by a quantitative fit to the experimental CL spectra using a sum of Gaussian line distributions. From the best fits, the presence of various transitions has been inferred. In Fig. 3 the single bands obtained from the fit are shown in each case as well as experimental data. The concordance is clearly seen. For the sake of comparison, the CL spectrum of an undoped p -GaSb sample is also shown [Fig. 3(a)]. The dominant transitions for the undoped sample occur at 775 and 796 meV. The 775 meV peak (usually referred as A band in the literature) has been attributed to a transition from conduction band to the native acceptor level V_{GaGaSb} .^{9,10} The 796 meV corresponds to the band–band transition. The sample with shortest diffusion time exhibits luminescence peaks at 744, 775, and 796 meV [see Fig. 3(b)]. The 744 meV peak is intrinsic to Te and has been attributed to transition from conduction band to an acceptor

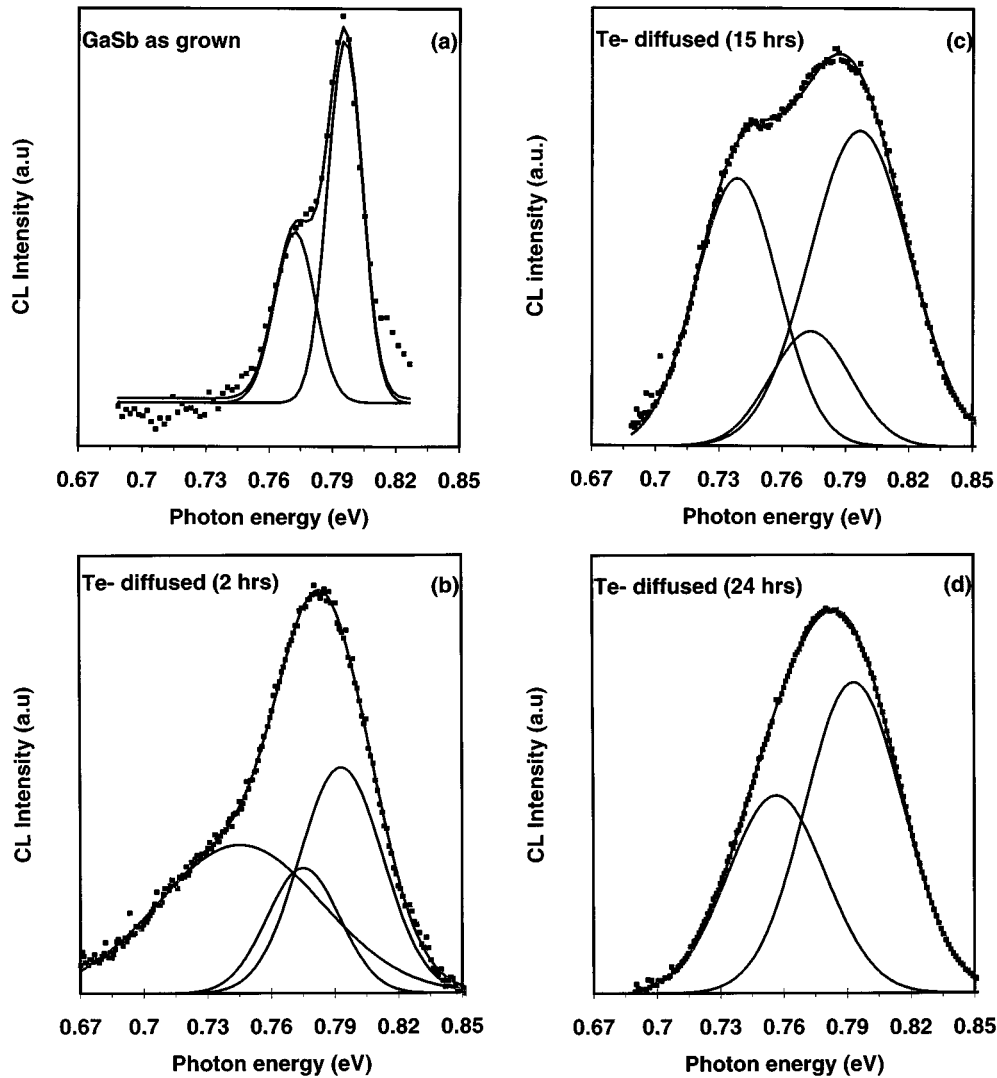


FIG. 3. CL spectra of GaSb at 77 K: (a) as-grown; (b)–(d) diffused with Te for 2, 15, and 24 h, respectively. Gaussian lines obtained from fitting and experimental points are shown.

state $V_{\text{Ga}}\text{Ga}_{\text{Sb}}\text{Te}_{\text{Sb}}$.³ The spatial distribution of this complex seems to be connected to dislocations as is shown in Fig. 2(a). With increase in Te concentration, the intensity of 744 meV peak increases [Fig. 3(c)] indicating the enhancement of the formation of the related acceptor center. This leads to increase self-compensation in the samples. An interesting result to be pointed out here is the CL spectrum of the sample with highest Te concentration [shown by Fig. 3(d)]. It is seen that the dominant defect transition in this sample occurs at 756 meV. The 796 meV peak is as usual present and the 744 meV transition almost disappears in all studied cases. The origin of the 756 meV transition (called B band in previous works) has not been clearly understood until now¹¹ and seems to arise from native complexes involving excess Ga vacancies ($V_{\text{Ga}}\text{Ga}_{\text{Sb}}V_{\text{Ga}}$).¹² In a recent CL investigation on Ga, Sb, and vacuum-annealed bulk undoped GaSb,⁷ we have found that the intensity of the 756 meV transition increases on annealing GaSb in Ga atmosphere. This observation cannot be explained by the increase of the proposed triple native acceptor center. In fact, the concentration of Ga vacancies should reduce on annealing in Ga atmosphere. On the other

hand, the acceptor center which can increase in the presence of excess Ga can be related to the Ga antisite or a complex involving the antisite defect. Thus, we attribute the 756 meV peak to a transition from the conduction band to an acceptor center involving Ga_{Sb} . The fact that the intensity of this peak increases in the Te-diffused sample for large diffusion times is due to increase in volatilization of Sb. This in turns results in excess Ga and is similar to the situation of annealing under Ga-rich conditions. The probability of formation of Ga_2Te_3 precipitates and the increase in concentration and size of precipitates as seen in the CL images of diffused samples with increasing diffusion time can also be explained by the presence of excess Ga. From the above discussion, it is clear that the dominant compensating acceptor varies with increase in diffusion time. This information is invaluable for simulation of Hall measurement data. Furthermore, the luminescence centers seen on Te diffusion in *p*-type samples (as in the present study) are much different than those seen after Zn diffusion in *n*-type samples.¹³ The asymmetric luminescence properties of the *p*–*n* junctions thus fabricated are

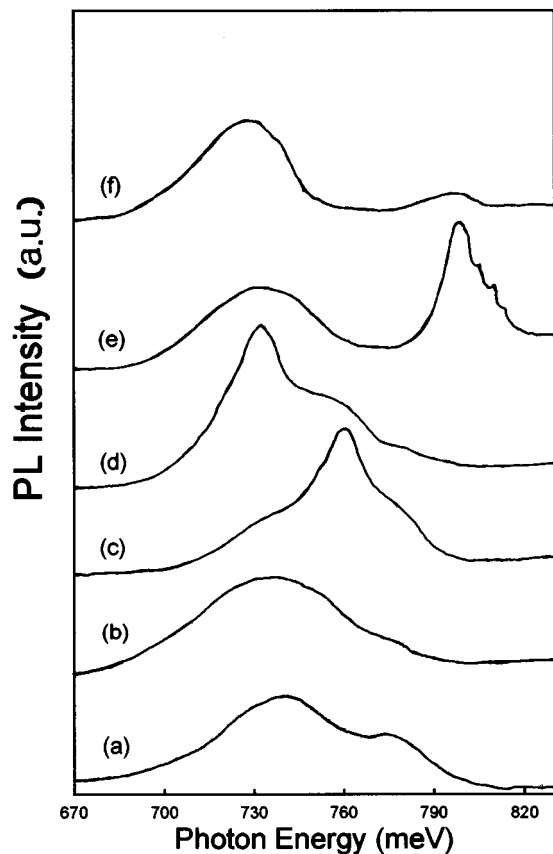


FIG. 4. PL spectra of Te-doped GaSb grown from (a),(b) stoichiometric melt; (c),(d) Ga-rich melt; and (e),(f) Sb-rich melt. The net donor concentrations are (a) 1.2×10^{17} , (b) 3.3×10^{17} , (c) 2.3×10^{17} , (d) 1.1×10^{18} , (e) 3.0×10^{17} , and (f) $1.3 \times 10^{18} \text{ cm}^{-3}$.

extremely important while designing electroluminescent devices with desired emission wavelength.

Figure 4 shows the PL spectra of various Te-doped bulk GaSb samples grown from stoichiometric, Ga-rich, and Sb-rich melts with net donor concentration in the range of 1.2×10^{17} and $1.3 \times 10^{18} \text{ cm}^{-3}$. Crystals grown from stoichiometric melts [Figs. 4(a) and 4(b)] mainly exhibit the 740 and the 777 meV transitions with relative intensity depending on the Te concentration. The PL spectrum of the sample grown from Ga-rich melt with low Te concentration [Fig. 4(c)] is similar to that of the diffused for longest time [Fig. 3(b)]. The dominant transition is around 760 meV (756 meV at 77 K) along with 740 and 777 meV peaks. With increase in Te concentration, the 740 meV transition increases and the 760 and 777 meV peak intensities become weak [Fig. 4(d)]. For the crystals grown from Sb-rich melts, the 777 meV intensity decreases as a result of reduction in native defect concentration. The dominant transition is at 740 meV along with partially resolved excitonic transitions at 800, 806, 808, and 810 meV as depicted in Fig. 4(e). With increase in Te concentration, the intensity of the 740 meV peak increase and the peak becomes broad [Fig. 4(f)]. Thus, with increase in Te concentration, the density of compensating acceptors also increases,

which has been verified from the theoretical simulation of experimental Hall measurement data (unpublished results). Furthermore, it should be noted that the samples grown from stoichiometric and Sb melts do not exhibit the 760 meV transition. This once again supports the assignment of the 756 meV transition to an excess Ga-related native defect. Finally, the difference in luminescence property of diffused and as-grown doped samples is worth comparing. Unlike in the diffused samples, the 744 meV peak increases with increase in Te concentration in the doped samples [compare Figs. 3(d) and 4(b)].

IV. CONCLUSIONS

From the present investigation it can be concluded that the defect complexes formed in GaSb are different during growth and postgrowth diffusion cycles. This is mainly due to the difference in the temperature at which the complex formation takes place.¹⁴ Our results support the attribution of the 760 meV band to a defect involving Ga_{Sb} . Furthermore, the type of defects formed in diffused samples is a function of diffusion time. This is a consequence of the precipitation processes as revealed by the CL images. In bulk crystals, the nature of defects formed depends on the melt composition. From a device fabrication point of view, this study provides useful insight into the two processes of doping and the resulting material properties. To evaluate the exact concentrations of various compensating centers and the mobility of diffused samples, rigorous Hall measurements on epitaxial films would be necessary. Further studies under Ga-rich, Sb-rich, and vacuum ambients could be highly interesting.

ACKNOWLEDGMENTS

P.S.D. thanks CSIR (India) for the award of the Senior Research Fellowship. This work was partially supported by the Instituto Nicolas Cabrera, UAM, Madrid, Spain, through a visiting scientist fellowship and by the DGICYT (Project No. PB93-1256), CICYT (IN 93-0012), and ESP-95-0148.

- ¹A. G. Milnes and A. Y. Polyakov, *Solid-State Electron.* **36**, 803 (1993).
- ²K. Nakashima, *Jpn. J. Appl. Phys.* **20**, 1085 (1981).
- ³A. I. Lebedev and I. A. Strel'nikova, *Sov. Phys. Semicond.* **13**, 229 (1979).
- ⁴P. S. Dutta, K. S. Sangunni, H. L. Bhat, and V. Kumar, *J. Cryst. Growth* **141**, 44 (1994).
- ⁵B. Méndez and J. Piqueras, *J. Appl. Phys.* **69**, 2776 (1991).
- ⁶P. S. Dutta, K. S. R. Koteswara Rao, H. L. Bhat, and V. Kumar, *Appl. Phys. A* **61**, 149 (1995).
- ⁷B. Méndez, P. S. Dutta, J. Piqueras, and E. Dieguez, *Appl. Phys. Lett.* **67**, 2648 (1995).
- ⁸J. Doerschel and U. Geissler, *J. Cryst. Growth* **121**, 781 (1992).
- ⁹M. Lee, D. J. Nicholas, K. E. Singer, and B. Hamilton, *J. Appl. Phys.* **59**, 2895 (1986).
- ¹⁰M. C. Wu and C. C. Chen, *J. Appl. Phys.* **72**, 4275 (1992).
- ¹¹W. J. Jiang, Y. M. Sun, and M. C. Wu, *J. Appl. Phys.* **77**, 1725 (1995).
- ¹²D. Weiler and H. Mehrer, *Philos. Mag. A* **49**, 309 (1984).
- ¹³A. Krier, M. K. Parry, and D. S. Lanchester, *Semicond. Sci. Technol.* **6**, 1066 (1991).
- ¹⁴S. Iyer, L. Small, S. M. Hedge, K. K. Bajaj, and A. Abul-Fadl, *J. Appl. Phys.* **77**, 5902 (1995).

Journal of Applied Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see <http://ojps.aip.org/japo/japcr/jsp>
Copyright of Journal of Applied Physics is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.

Journal of Applied Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see <http://ojps.aip.org/japo/japcr/jsp>