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Photoluminescene study acceptor defects in lightly doped n type GaSb single crystals

Guiying Shen[1], Youwen Zhao[1, 2], Yongbiao Bai[1, †], Jingming Liu[1], Hui Xie[1], Zhiyuan Dong[1], Jun Yang[1], and Ding Yu[1, 2]

[1]Key Laboratory of Semiconductor Materials Science and Beijing Key Laboratory of Low-Dimensional Semiconductor Materials and Devices, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

[2]Center of Materials Science and Opto-Electronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Lightly Te-doped GaSb samples grown by the liquid encapsulated Czochralski (LEC) method have been studied by Hall measurements and low-temperature PL spectroscopy. The results suggest that acceptor-related antisite is the dominant defect in n-type GaSb with low Te-doping concentration. As the Te concentration increases, gallium vacancy related defects become the main acceptor. A new band of around 665 meV is observed in the GaSb sample with the lowest Te-doping concentration. The variation of the acceptor defects and their influence on the electronic and optical property on the n-GaSb single crystal are discussed based on the results.

Key words: Te-doped GaSb; Hall; native defects; PL

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1. Introduction

Gallium antimonide (GaSb) is an important semiconductor material for fabricating infrared opto-electronic devices and thermophotovoltaic cells. In particular, GaSb substrate has been successfully applied to manufacture type-II InAs/GaSb superlattice infrared detectors operating from mid to long wavelength[1, 2], which makes it important in the next generation infrared imaging system[3]. High below gap infrared transmission is expected for the GaSb substrate that is used for the infrared detectors[3, 4]. However, high concentration of native acceptor defects exist in as-grown and annealed GaSb single crystals[5, 6], which makes it exhibits strong below gap absorption[6–10]. Consequently, it is necessary to suppress the formation of the native acceptor defects in GaSb and also improve the structure and electrical properties.

GaSb single crystals can be grown by three methods: the Czochralski technique (CZ), vertical gradient freeze (VGF) and liquid encapsulated Czochralski technique (LEC)[11–13]. Generally, as-grown GaSb single crystals usually have p-type conduction with carrier concentration of (1–3) × 10^{17} cm^{-3}[10, 14], irrespective of the growth method and technique due to the existence of gallium vacancy (V_{Ga}) and gallium antisite (Ga_{Sb}), which are both doubly ionizable[8, 9]. At present, LEC is used for commercial mass-production of high quality GaSb single crystal. The V_{Ga} and Ga_{Sb} defects serve as doubly ionizable native acceptors and generate some below gap absorption, which influence the optical properties of GaSb. A proper concentration of Te-doping can compensate the native acceptor defects in the maximum extent and improve the transmission of GaSb[15, 16].

In this paper, photoluminescence (PL) spectroscopy has been used to study defects in as-grown and lightly Te-doped GaSb single crystals. Special attention is paid to the variations of native acceptor defect with the change of Te-doping concentration and their combined influences on the properties of GaSb.

2. Experiments

(100) GaSb wafers with 750 μm thickness were sliced from lightly Te-doped GaSb bulk single crystal ingots grown by LEC technique. The wafers were polished on both sides for the optical measurement. The electrical properties, including carrier concentration and mobility were investigated through a Hall measurements system at room temperature. The PL spectra of the samples were obtained at 10 K by using a Bruker Vertex 80 FTIR equipped with an InSb detector. The excitation power of the PL spectra was 100 mW.

3. Results and discussion

The electrical parameters of GaSb samples with different Te-doping concentration are listed in Table 1. For n-type GaSb samples, the free carrier concentration varies from 1.66 × 10^{16} to 1.38 × 10^{17} cm^{-3} and the mobility changes from 2.34 × 10^3 to 3.34 × 10^3 $cm^2/(V{\cdot}s)$. It has been found that the mobility increases with the increasing carrier concentration due to the compensation of Te atoms. The native defects that exist in as-grown GaSb, e.g. V_{Ga} and Ga_{Sb}, have a negative effect on the electron transition process and decrease the mobility. In Te-doped GaSb samples, the Te atoms are very likely to occupy the sites of vacancy defects. Thus, the ionized impurity scatting is suppressed and the mobility will increase with the increasing Te-doping concentration. However, when it turns from sample 6 to 7, the mobility decreases from 3.34 × 10^3 to 3.24 × 10^3 $cm^2/(V{\cdot}s)$, due to the stronger free carrier scatting exists in sample 7. Samples 8 and 9 have p-type conduction with

Correspondence to: Y B Bai, baiyongbiao@semi.ac.cn
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Table 1. Hall results of n-type Te-GaSb sample at room temperature.

Sample No.	Mobility ($cm^2/(V\cdot s)$)	Carrier concentration (cm^{-3})	Type
1	2.34×10^3	1.66×10^{16}	n
2	2.83×10^3	2.79×10^{16}	n
3	2.94×10^3	5.24×10^{16}	n
4	2.96×10^3	6.63×10^{16}	n
5	3.04×10^3	7.84×10^{16}	n
6	3.34×10^3	1.14×10^{17}	n
7	3.24×10^3	1.38×10^{17}	n
8	6.41×10^2	1.41×10^{17}	p
9	7.39×10^2	1.14×10^{17}	p

Table 2. The PL peak position and related transition of GaSb reported in the literature.

Energy (meV)	Transition	Quota
812	Band gap	Ref. [19] (4.2 K)
810	Free exciton	Ref. [20] (20 K)
808	Excitonic transition	Ref. [18] (19 K)
802	Donor-acceptor transition	Ref. [19] (4.2 K)
797	Excitonic transition	Ref. [18] (19 K)
796, 792	Exciton band to $(V_{Ga}\,GaSb)^0$	Ref. [19] (4.2 K)
781	C-$(V_{Ga}\,GaSb)^0$	Ref. [19] (4.2 K)
777	D^+-$(V_{Ga}\,GaSb)^0$	Ref. [19] (4.2 K)
765	LO phonon replica of 796 meV transition	Ref. [18] (19 K)
760	Acceptor B	Ref. [18] (19 K)
756	Exciton band to GaSb	Ref. [5] (10 K)
746, 740	LO phonon replica of 777 meV	Ref. [19] (4.2 K)
738	C-$(V_{Ga}\,GaSb\,Te_{Sb})$	Ref. [18] (19 K)
710	C-$(V_{Ga}\,GaSb)$	Ref. [19] (4.2 K)
682	LO phonon replica of 710 meV	Ref. [19] (4.2 K)

relative low mobility. The low mobility of sample 8, which is prepared as an undoped wafer, can be attributed to the high concentration of native acceptor defects. The mobility of sample 9, which is lightly Te-doped GaSb, is higher than that of sample 8 because of the light degree of compensation of Te atoms. The electrical properties of samples 8 and 9 are listed in Table 1 as a comparison to find the transformation of the defects concentration and properties. The charge-neutrality condition can be written as

$$n_0 + N_A^- = N_{D_1}^+ + N_{D_2}^+ + p_0, \tag{1}$$

where n_0 denotes the electron concentration, N_A^- is the concentration of ionized acceptors, $N_{D_1}^+$ and $N_{D_2}^+$ are the concentration of ionized Te atoms and another donor, p_0 is the hole concentration. In p-type GaSb, holes are the main carrier and electrons make little contribution to carrier concentration. Thus, the electric charge balance equation can be simplified as,

$$N_A^- = p_0, \tag{2}$$

i.e. high concentration of native acceptor (V_{Ga} and Ga_{Sb}) exhibits in p-type GaSb. In n-type GaSb, electrons become the main carrier, while the concentration of holes and ionized acceptors can be ignored. Te atoms ionized as donors play a leading role in compensating the native acceptor defects, forming the main ionized acceptors in the structure of $V_{Ga}Te_{Sb}$.

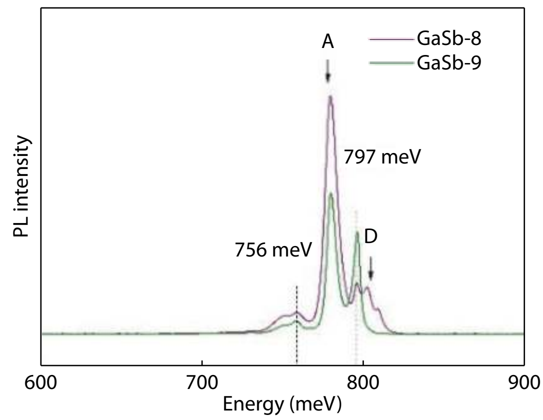

Fig. 1. (Color online) PL spectra of p-type GaSb samples measured at 10 K.

Photoluminescene (PL) measurement can be effectively used to study the details of defects in a material. More information about the electron and exciton transitions can be obtained from PL spectra measured at low temperature. It is found that four kinds of absorption process exhibit in GaSb single crystals[17]. It is also reported that the main PL peak (named A) around 777 meV for the as-grown GaSb is considered to be related to the native acceptor defects V_{Ga} and Ga_{Sb}. For the as-grown and lightly Te-doped p-type samples, there are two peaks around A located at 756 and 797 meV, respectively. The PL peak at 756 meV is attributed to the transition from conduction band to the acceptor center. The 797 meV peak corresponds to the neutral acceptor, whose concentration is in a unity of opposites with that of native acceptor defects. For n-type GaSb, a band around 700 meV (named C) relating to the native double acceptor grows and its intensity increases with the decreasing carrier concentration. Nevertheless, it will disappear when the carrier concentration exceeds 7×10^{17} cm^{-3} due to the high compensation. The peak around 800 meV (named D) is referred to as a free-to-bound recombination and integrates with band A. For Te-doped GaSb, a peak named T appears and it becomes the dominate peak as the doping level increases. It is found that this peak corresponds to free-to-bound recombination of Te atoms and complex defects ($Te_{Sb}V_{Ga}Ga_{Sb}$). There are some other peaks at 805, 803, 800, 796 meV which are related to the transition from excitons bound to the neutral native complex defect ($V_{Ga}Ga_{Sb}$). The related transition mechanism of the PL spectra is summarized in Table 2[18–20].

Fig. 1 shows the PL spectra of the p-type GaSb samples. It can be seen that the intensity of the peak A and the peak at 756 meV is lower than that of sample 9. While the intensity of the 797 meV peak increases after doping Te atoms lightly. It has been reported that band A is related to the V_{Ga} and the peak at 756 meV is attributed to Ga_{Sb}, inferring that the V_{Ga} and Ga_{Sb} defects will be restrained by doping with Te atoms. The increasing intensity of the 797 meV peak indicates a decreasing of concentration of native defects[5]. It should be noted that some other peaks around 810 meV are related to free-exciton transitions in GaSb, although these peaks are not listed above due to their weakness. For the n-type GaSb samples shown in Figs. 2–4, peaks A and D merge into one peak and

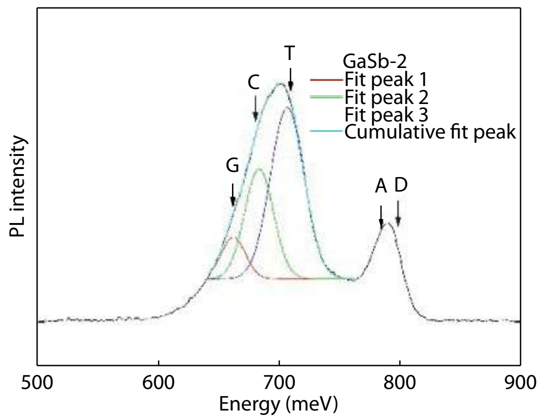

Fig. 2. (Color online) PL spectra of sample 2 at 10 K.

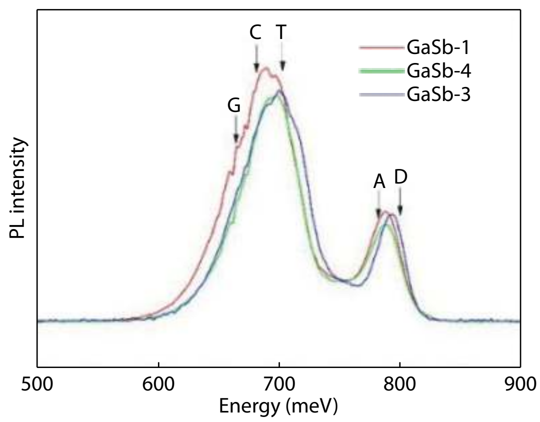

Fig. 3. (Color online) PL spectra of samples 1, 3 and 4 at 10 K.

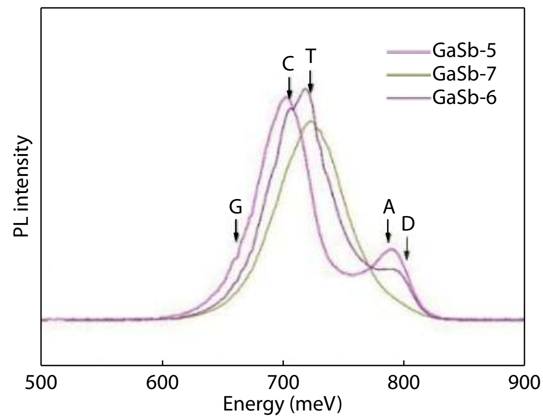

Fig. 4. (Color online) PL spectra of samples 5, 6 and 7 at 10 K.

the intensity of the new peak becomes weaker as the carrier concentration increases. It almost disappears in sample 7 with a carrier concentration of 1.38×10^{17} cm^{-3}, which can be attributed to the adequate Te atoms that compensate the native acceptor defects. The peak at 756 meV also disappears with the increase of Te-doping concentration, which indicates that the Ga_{Sb} defects have been annihilated. It is easier for Te impurities to occupy the sits of Ga_{Sb} than V_{Ga}. Thus, V_{Ga} acceptors become the main acceptor defects in the Te-doped samples.

In Figs. 2–4, a broad peak with several resolved peaks shows up and it dominates the spectrum of the Te-doped GaSb with the carrier concentration below 1.4×10^{17} cm^{-3}. In the lightly Te doped GaSb samples, the broad band incorporates a new peak, named peak G, around 664 meV, which is related to the complex defects consisting of totally ionized Te atoms and partial compensated native acceptor defects, such as V_{Ga} and Ga_{Sb}. As the doping concentration increases, more native acceptor defects are compensated by the ionized Te atoms. Thus, the PL peak of the complex defects becomes weaker as the Te-doping concentration increases. It is expected that a native acceptor defect will be compensated completely when the doping concentration exceeds the critical value, resulting in annihilation of the complex defects.

Table 3. The position (meV) and intensity (a.u.) of resolved peak G, C and T.

Sample No.	Peak position	Strength of peak G	Peak position	Strength of peak C	Peak position	Strength of peak T
1	665	0.65	683	1.26	703	1.73
2	664	0.52	683	1.43	706	1.68
3	664	0.43	685	1.52	708	1.53
4	665	0.42	686	1.58	707	1.56
5	666	0.12	692	0.92	712	1.59
6	–	–	700	0.83	721	1.76
7	–	–	712	0.75	732	1.98

Table 3 shows the position and strength of peaks G, C and T which are resolved from the integrated broaden peak (the resolved peak A and D are not listed due to their weakness). Peak G shows relatively high strength for sample 1 and it then drops rapidly with the increase of Te-doping concentration. Peak G almost disappears, when it turns to sample 6 and 7. The intensity of peak C shows a little increase from sample 1 to 4 and then drops rapidly as the carrier concentration increases. The increase can be explained as the change of occupation state of the residual acceptors which leads to the moving up of Fermi level[17]. The decreasing intensity is caused by the reduction of the native double acceptors as the doping level increases. In the Te-doped samples, band T becomes the dominant peak. The intensity of peak T shows a slight decrease from sample 1 to 4 and then increases from sample 5 to 7. The existence of the complex defects corresponding to peak G may be the reason for the variation of peak C. This can be further confirmed from the decrease of peak G. As the carrier concentration increases, the native acceptor defects have been compensated and the Te-related complex defects become the main optical motivation. The defects character has been changed from native acceptors to Te atoms related complexes in GaSb samples. In addition, from Eq. (1), as the carrier concentration increases, the n_0 keeps increasing while the N_A^- decreases, which indicates the decline of the native acceptors including V_{Ga} and Ga_{Sb}. At the same time some defects related to Te atoms appear. It can be seen the broad peak containing C and T shows a blue shift about 30 meV as the carrier concentration increases from 1.66×10^{16} to 1.38×10^{17} cm^{-3}. It can be concluded that the low energy tails caused by the heavy doping effects appear, leading to the growth of the high-energy side of the bands. Thus, the blueshifts[17] of the peak C and T have been observed.

Vlasov has pointed out that the FWHM of peak C is proportional to the defect concentration[9]. It can be seen from the figure that the FWHM of peak C decreases from sample 1 to sample 5, indicating that the concentration of the native double acceptors decreases with the increase of Te compensation. However, in samples 6 and 7, the FWHM of PL peaks are larger than that of sample 5, which can be attributed to the decrease of band C and the increase of band T. Moreover, the broadening of the optical absorption caused by the introducing of impurity energy level with excessive carrier could also be responsible for this result. In the relatively high-energy region, there is a broad and weak band from 730 to 777 meV containing B (760 meV), A-LO (749 meV), U (743 meV) and B-LO (732 meV)[20]. Peaks A and B are related to the deep acceptors. A-LO and B-LO are in connection with LO phonon replicas of peaks A and B. All of these bands decrease from sample 1 to 3 and then increase from sample 3 to 5, because the concentration of deep acceptors increase with the carrier concentration. in samples 6 and 7, the related band disappears due to the excessive Te atoms which have compensated the deep acceptor. None of these peaks are pointed out in the figures due to their weakness.

4. Conclusion

The electrical and optical properties of the as-grown and lightly Te-doped GaSb samples have been investigated through Hall measurement and PL spectra. Native acceptor defects are suppressed with the increasing Te-doping concentration. The PL spectra show good correlation between the Te-doping concentration and the intensity of the defect related peaks. In the native acceptor defects Ga_{Sb} and V_{Ga} that are compensated by Te atoms and Ga_{Sb} related peaks almost totally disappear when V_{Ga} defects become the main acceptor defects. A new band around 665 meV appears in the samples with carrier concentration below 7.84×10^{16} cm^{-3}. It can be argued that this band corresponds to the complex defects consisting of ionized Te atom, native acceptor defects V_{Ga} and Ga_{Sb}. More native acceptor defects are compensated by the ionized Te atoms, as the doping concentration increases. It is also found that native acceptor defects are compensated completely when the doping concentration exceeds the critical value, resulting in annihilation of the complex defects.

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