N-type GaSb single crystals with high below-band gap transmission*

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Te-doped GaSb single crystals are studied by measuring Hall effect, infrared (IR) transmission and photoluminescence (PL) spectra. It is found that the n-type GaSb with IR transmittance can be obtained as high as 60% by the critical control of the Te-doping concentration and electrical compensation. The concentration of the native acceptor-associated defects is apparently low in the Te-doped GaSb compared with those in undoped and heavily Te-doped GaSb. The mechanism for the high IR transmittance is analyzed by considering the defect-involved optical absorption process.

Keywords: Te-doped GaSb, infrared transmission, native defects, PL

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1. Introduction

Gallium antimonide (GaSb) is an important III–V semiconductor material used for manufacturing infrared detectors, laser diodes, high-frequency devices, superlattices and LEDs.[1–3] Recently, one of its most important applications is to serve as a substrate material for infrared detectors such as type-II superlattices InAs/InAsSb,InAs/GaSb,[4,5] especially in the focal plane array (FPA).[6,7] The third-generation infrared FPAs have extensive applications in both military and civilian fields, such as infrared night vision system, object identification and atmosphere surveillance. However, there exists very strong absorption in the GaSb substrate under backside illumination configuration when the substrate is not completely removed in fabricating quad FPA, thus it is necessary to reduce the absorption of GaSb substrate and enhance its below-band gap transmission. For this purpose, the IR transmission of GaSb should be as high as possible. Unfortunately, as-grown GaSb usually exhibits p-type conduction caused by native gallium vacancies (V_{Ga}) and gallium anti-sites (Ga_{Sb}) at a concentration of 10^{17} cm^{-3}.[8,9] The V_{Ga} and Ga_{Sb} defects serve as doubly ionizable native acceptors,[10,11] generating strong below-band gap absorption and electrical compensation of n-type doping.[12]

In principal, the main absorption mechanism of GaSb is inter-valence band absorption based on the transitions from the light-hole to the heavy-hole band in the p-type GaSb, while free-carriers, inter-valley conduction band electron absorption mechanism dominates in n-type GaSb.[13,14] Therefore, GaSb wafer with high transmission can be obtained through a proper Te doping compensation which not only compensates for the vacancies and native acceptors but also keeps carrier absorption as low as possible. Liquid encapsulated Czochralski (LEC) technique[15] is a conventional crystal growth method which is suitable for the mass-production of high quality GaSb single crystal. Its drawback is that a high concentration of native acceptor defect is easily formed in the growth process. In this paper, we focus on the enhancement of IR transmission of GaSb substrate material obtained from LEC growth method with tellurium doping compensation. Optical property of Te-doped GaSb has been studied by several groups by using crystal samples grown by horizontal Bridgman (HB),[16–19] solution growth method,[20,21] etc. In this paper, various lightly Te-doped n-type LEC-GaSb samples are used to study the associated mechanism and obtain high transparency substrates through controlling the doping concentrations and compensating for the native acceptor defects.

2. Experiment

Te-doped GaSb bulk single crystal ingots with (100) orientation were grown by LEC technique. The (100) wafers each with 750-μm thickness were sliced and polished on both sides for measuring the infrared optical properties. The electrical properties, such as carrier concentration, mobility and doping condition were investigated through a Hall measurements system at room temperature. The IR transmittances of the samples were measured by an FTS-60V Fourier transform infrared spectrometer system (FTIR). Defects in the samples were investigated by PL spectra obtained at 77 K by using a Bruker Vertex 80 FTIR equipped with an InSb detector. The excitation power of the PL spectra was 100 mW.

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3. Results and discussion

In order to obtain GaSb single crystal with good below-band gap transmission, the relationship between doping concentration, defect concentration and IR transmittance needs to be identified. The transmittance and absorption coefficient can be obtained through the following formula:[13]

$$T = \frac{(1-R)^2 \mathrm{e}^{-\alpha t}}{1-R^2 \mathrm{e}^{-2\alpha t}}, \tag{1}$$

where α is the absorption coefficient, t is the thickness of the sample, and R is the reflectivity that comes from the formula

$$R = \left(\frac{n-1}{n+1}\right)^2, \tag{2}$$

where n is the refractive index which has a constant of 3.8 for GaSb when the optical wavelength $\lambda < 20$ μm. The transmittance is mainly related to the absorption coefficient and thickness, the t can be considered as constant because all the samples possess the same thickness, thus the absorption coefficient α becomes the only influencing factor for the transmission. Chandola *et al.* have discussed the absorption mechanisms in semiconductors, the absorption coefficient can be expressed as[13]

$$\alpha = \alpha_{\mathrm{FCAe}} + \alpha_{\mathrm{FCAh}} + \alpha_{\mathrm{IVB}} + \alpha_{\mathrm{CB}}. \tag{3}$$

Each coefficient item corresponds to one absorption mechanism. The α_{FCAe} relates to the free carrier absorption by free electrons, α_{FCAh} the free carrier absorption by free holes, α_{IVB} the inter-valence band absorption by holes, α_{CB} the inter-valley conduction band absorption by electrons. The α_{IVB} combines three absorption mechanisms

$$\alpha_{\mathrm{IVB}} = \alpha_{\mathrm{lh-hh}} + \alpha_{\mathrm{so-lh}} + \alpha_{\mathrm{so-hh}}, \tag{4}$$

which relate light hole to heavy hole, split-off to light hole and split-off to heavy hole transitions absorption. Kahn[14] and Kane[22] have discussed the three mechanisms, and the only effective transition came from light hole to heavy hole in GaSb. Thus α_{IVB} can be simplified into $\alpha_{\mathrm{lh-hh}}$. However, in the n-type sample where $n > 1\times10^{16} \gg n_i$, $p = n_i^2/n \approx 10^8$, there are barely free holes and the hole concentration can be ignored. Thus in our Te-doped GaSb single crystal wafer samples, the free-hole absorption α_{FCAh} can be ignored and the transition from light hole to heavy hole can be disregarded too, so we remove α_{IVB}. Thus α_{FCAe} can be simplified into the following formula:[23]

$$\begin{aligned}\alpha_{\mathrm{FCAe}} &= \left(\frac{e^3}{4\pi^2 c^3 m_0^3 \varepsilon_0}\right)\left(\frac{1}{n\left(\frac{m^*}{m_0}\right)^2}\right)\left(\frac{\lambda^2}{\mu}\right)N \\ &= KF_{\mathrm{CAe}}\lambda^m, \end{aligned} \tag{5}$$

where N is the carrier concentration, $K \propto N/\mu$ and λ is the wavelength. Becker *et al.*[24] and Lorenz *et al.*[25] gave the expression for α_{CB} as follows:

$$\alpha_{\mathrm{CB}} = K_{\mathrm{CBV}}(1.24/\lambda - E_0)^{1/2}, \tag{6}$$

where λ is the wavelength, K_{CBV} and E_0 depend on the carrier concentration. The absorption increases with increasing carrier concentration, and decreases with increasing wavelength. Thus the absorption coefficient can be simplified into

$$\alpha = \alpha_{\mathrm{FCAe}} + \alpha_{\mathrm{CB}}, \tag{7}$$

so the absorption mainly relates to free carrier concentration and inter-valley conduction band in the Te-doped GaSb sample. In addition, acceptor-defects-related absorption should be considered too.

In the present work, Te-doped GaSb samples are chosen for the investigation in order to obtain the IR transmission as high as possible. As has been mentioned, the main absorption mechanisms are inter-valley conduction band absorption and the free electron absorption in the n-type GaSb. From the formula, we know that the main absorption mechanism is inter-valley conduction band absorption in a range from 2.5 μm to 5 μm, there is barely no absorption for inter-valley conduction band absorption after 15.5 μm and the only absorption mechanism is electron free carrier absorption. For the Te-doped n-type GaSb sample, the concentrations of residual holes, vacancies and native acceptor defects fall and the transmission increases because of the Te doping compensation. However, when the Te content increases too much (heavily Te-doped), beyond 1×10^{17} cm^{-3} for instance, the free carrier absorption becomes the main constrained element and the absorption increases promptly due to the excessive free carriers, resulting in a rapid transmission drop. Therefore there should be an appropriate Te doping content that not only compensates for the residual holes, vacancies and native acceptor defects but also generates suitable free carrier concentrations to keep the minimum absorption. Electrical properties of GaSb samples with different Te doping content are shown in Table 1. The free electron concentrations of the samples vary from 1.65×10^{16} cm^{-3} to 6.5×10^{16} cm^{-3}, while the mobilities change from 1.57×10^3 cm^2/V·s to 3.01×10^3 cm^2/V·s. All the samples exhibit a relatively high mobility level.

Table 1. Hall results of n-type Te-GaSb samples at room temperature.

Sample No.	Mobility /(cm^2/V·s)	Carrier concentration/cm^{-3}	Type
1	2.34×10^3	1.65×10^{16}	n
2	1.57×10^3	1.81×10^{16}	n
3	2.82×10^3	2.78×10^{16}	n
4	3.00×10^3	5.23×10^{16}	n
5	3.01×10^3	6.50×10^{16}	n

Figure 1 shows the FTIR transmission spectra with different Te doping concentrations. The n-type samples with carrier concentration beyond 7×10^{16} cm^{-3} are not in consideration because of the relatively high carrier concentration and low mobility. Samples 1–5 are shown in Fig. 1, the transmission attains the maximum at the intrinsic band edge then turns down slowly with wavelength increasing. Samples 4 and 5 show high transmittances are all above 50% at the intrinsic band edge, and the transmissions are not saturated with wavelength increasing but still keep high levels. Samples 2 and 1 show maximum transmittances above 55% from the intrinsic band edge to 10 μm, it is higher than 30% with the wavelength less than 20 μm, which show good IR transmission property. The spectra show that sample 3 possesses the maximum IR transmittance 60% between intrinsic band edge and 8 μm, above 30% from 8 μm to 20 μm, indicating a very high transmission level.

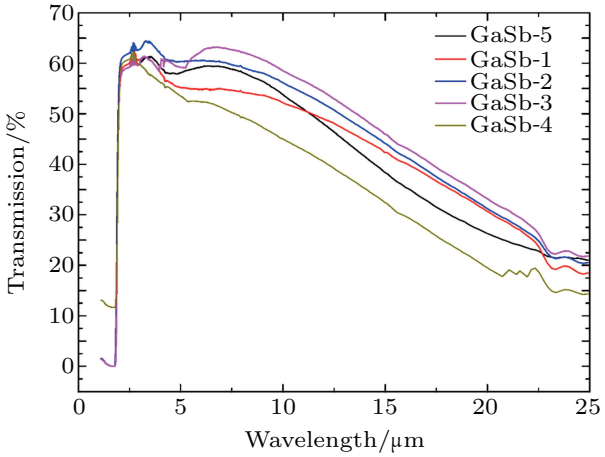


Fig. 1. (color online) Absorption spectra of lightly doped n-type LEC-GaSb samples.

From Eq. (5), it is the ratio N/μ that influences α_{FCAe}. So it seems that sample 1 should have the lowest absorption since its N/μ is a minimum value, then followed with samples 3, 2, 4, and 5. The α_{CB} value increases with free carrier concentration increasing, so sample 1 should possess a minimum α_{CB} theoretically, followed by samples 2, 3, 4, and 5. However, figure 1 shows that sample 3 possesses the maximum transmittance and sample 2 has transmittance higher than sample 1. Thus, in addition to the above-mentioned absorption process, absorption from native acceptor defects must be considered and it can be inferred that GaSb-3 possesses the minimum vacancies, defects and native acceptors defects with the help of Te atoms compensation. The GaSb-5 shows a higher transmission than GaSb-4, which indicates that GaSb-5 possesses the lower native acceptor defects too. This is because the carrier concentration of GaSb-5 is higher than GaSb-4 while the mobility keeps uniform, which can be seen in Table 1, thus GaSb-4 has higher acceptor compensation and native acceptor defects which lead to the lower transmission. As can be seen from the FTIR, the LEC GaSb samples can obtain a broad and high IR transmission range between 2 μm and 20 μm through Te-doped compensation when the carrier concentration is 2.78×10^{16} cm^{-3}.

Figure 2 show the 77-K PL spectra of the LEC-GaSb samples listed in Table 1. The carrier concentration should not be higher than 1×10^{17} cm^{-3} for high IR transmission when GaSb serves as a substrate for back-side illumination detectors.[15] Bignazzi *et al.*[26] proved four main peaks which can be seen in the PL spectra in Fig. 2: Peak A at 774 meV, peak C around 710 meV, peak D at 805 meV and peak T at about 802 meV. Peak A is related to the native acceptor defects V_{Ga} and Ga_{Sb},[27,28] and its intensity is relatively weak and has little influence on the spectra due to the almost complete ionization of the acceptor at 77 K. The peak D refers to free-to-bound recombination and shows weak intensity too.[26] It is noted that a strong broad peak with two resolved peaks C and T dominates in the spectra of Te-doped GaSb samples. The peak C is related to recombination of the native double acceptors and its intensity increase with carrier concentration increasing. The peak T usually appears in Te-doped GaSb sample and becomes a dominant peak with doping level increasing. It may come from free-to-bound recombination that relates to Te atoms and complex defects.[29] There should be some other emissions[30] such as 803, 800, and 796 meV which are related to the transitions from activation bound to the neutral native complex defect $(V_{Ga}Ga_{Sb})^0$, however most of these peaks almost disappear, all these indicate less defects and vacancies in the samples.

Vlasov *et al.*[11] proved that the full width at half maximum (FWHM) of peak C is related to native defect concentration and increases with defect concentration increasing. Figure 2 shows that sample 5 exhibits the maximum FWHM and intensity of peak C, then followed by sample 4. This fact implies that the two samples contain more native defects than other samples. Sample 1 shows relatively small FWHM, but slightly larger than sample 3, indicating more native defects in the sample. As can be seen from this figure, sample 3 demonstrates the minimum FWHM, indicating the lowest native defect concentration. In addition, it also has the lowest intensities of peaks A and D, suggesting less native acceptors V_{Ga}, Ga_{Sb} and free-to-bound recombination. It should be noted that there are little red shifts of the main peaks, which are due to the difference in carrier concentration. As has been described, sample 3 shows the best PL property, which indicates fewer residual holes, native acceptors and defects. Thus we can conclude that with the help of appropriate Te doping, the concentration of the defects can be suppressed and a better optical property could be obtained.

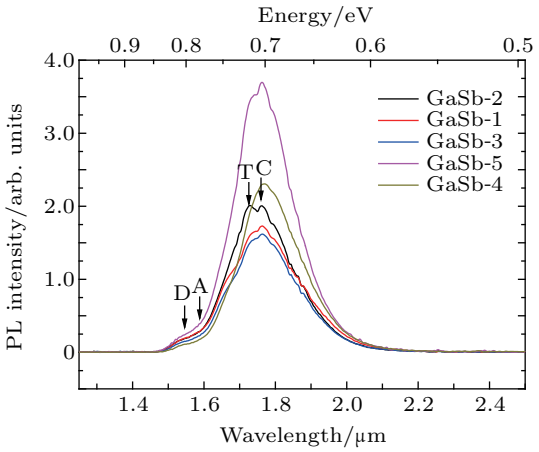


Fig. 2. (color online) PL spectra of the lightly doped n-type LEC- GaSb samples.

4. Conclusions

Te-doped GaSb single crystal with a carrier concentration of 10^{16} cm^{-3} and good mobility has below-band gap transmittance as high as 60%. The high transmittance is ascribed to low absorption relating to a very low native acceptor concentration and weak free carrier absorption due to the low carrier concentration.

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