Thermally induced native defect transform in annealed GaSb*

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Undoped p-type GaSb single crystals were annealed at 550–600 °C for 100 h in ambient antimony. The annealed GaSb samples were investigated by Hall effect measurement, glow discharge mass spectroscopy (GDMS), infrared (IR) optical transmission and photoluminescence (PL) spectroscopy. Compared with the as-grown GaSb single crystal, the annealed GaSb samples have lower hole concentrations and weak native acceptor related PL peaks, indicating the reduction of the concentration of gallium antisite related native acceptor defects. Consequently, the below gap infrared transmission of the GaSb samples is enhanced after the thermal treatment. The mechanism about the reduction of the native defect concentration and its influence on the material property were discussed.

Keywords: GaSb, annealing, defect, Hall effect measurement

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1. Introduction

GaSb is a technologically important III–V semiconductor substrate material, has a direct band gap of 0.725 eV at 300 K and 0.81 eV at 2 K, and a cubic lattice constant of 6.095 Å. Its lattice parameter matches the solid solutions of various ternary and quaternary III–V compounds whose band gaps cover a wide spectral range from 0.3 eV to 1.58 eV (0.8–4.3 μm).[1,2] GaSb is of interest as a low band gap material with applications in devices operating in the infrared range.[3] GaSb-based device structures have shown potential for applications in infrared detectors with high quantum efficiency,[4–6] diode lasers with low threshold voltage,[7–10] and high-efficiency thermophotovoltaic (TPV) cells.[11–13] The detection of longer wavelengths, 8–14 μm, is also possible with inter-subband absorption in antimonide-based superlattices.[14,15]

Undoped GaSb is always p-type in nature with a residual acceptor concentration of approximately 10^{17} cm^{-3} at room temperature. The high carrier concentration has been often attributed to native lattice defects or antistructure defects related to gallium vacancies (V_{Ga}) and gallium in antimony site (Ga_{Sb}) with doubly ionizable nature. Hall measurements with Li-diffused samples indicate that the acceptor should be doubly ionizable with ionization energies of 34.5 meV and 102 meV for the first and the second hole energy levels, respectively, by photoluminescence (PL) experiments at 2 K.[16,17] The existence of the native acceptor defects in GaSb gives rise to strong below gap absorption and electrical compensation for n-type doping,[18–20] which is a disadvantage for the optoelectronic device application. Studies have been mainly devoted to understanding the nature and the origin of the residual acceptors, which are the limiting factors for both fundamental studies and device applications, over the last five decades. Nonstoichiometric growth conditions have been used to reduce the acceptor concentration and increase the hole mobility. To reduce the level of the natural acceptors and increase the hole mobility, many intensive studies have been conducted, including the low-temperature growth from Ga solvent and the growth from Sb-rich solution.[21–24]

In this paper, the undoped GaSb samples are annealed in Sb ambient for a long duration. The GaSb samples are analyzed by Hall effect measurement, infrared (IR) optical transmission and photoluminescence spectroscopy respectively. A reduction of the native defect concentration is observed after the thermal treatment and its mechanism is analyzed based on the migration of gallium atoms and transformation of the antisite defect.

2. Experiment

Undoped GaSb ingots were grown by the liquid encapsulated Czochralski (LEC) method. High purity (99.9999%) Ga and Sb metals were used as the starting materials. The GaSb wafers used in our studies were cut perpendicular to the growth direction [100] and prepared in double in order to carry out the study on (i) as-grown and (ii) annealed wafers. The wafers

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were cut into small pieces for annealing. The quartz tube used for annealing was soaked in alcohol and aqua regia for 1 h and cleaned with deionized water. Then the tube was baked by putting in a drying oven. A small quantity of high purity Sb raw material granule was put at the end of the tube to provide ambient antimony for the annealing. The amount of the Sb raw material was computed for maintaining an atmospheric pressure in the tube during the annealing. The undoped GaSb samples were put along the axis to avoid covering each other in the tube. After placing the samples, the tube was pumped to a vacuum for 30 min to eliminate any trace of impurity gas present in the source, then sealed and positioned in a horizontal thermal annealing oven. The tube was situated in a constant temperature zone with the temperature rising from room temperature to 500 °C (550 °C or 600 °C) in 2 h. The temperature was controlled by a program and measured by a thermocouple. The samples were subsequently annealed at the temperature of 500 °C (550 °C or 600 °C) for 100 h followed by slow cooling for 10 h.

The chemical mechanical polishing was applied to the as-grown and the annealed samples. All the samples were polished on both sides with a commercially available polishing solution to achieve mirror shining surfaces on both sides. In this way, we obtained double-sided polished samples with almost the same thickness of 500 μm. Each of the samples (1 cm×1 cm in size) was checked by optical and electrical measurements in order to ensure the comparability of the results. The Hall measurement was used to study the change of the carrier concentration in the annealed samples. The Hall measurement was performed using an EGK Hall measurement system at 300 K. The thickness of the samples was 520±5 μm. Glow discharge mass spectrometry (GDMS) provided reliable quantitative concentrations for most elements with a resolution up to 0.001 ppm and was used to check the impurity content in the samples. The unit of the data listed in Table 2 is ppm. Photoluminescence (PL) spectroscopy studies were conducted to investigate the structural changes in the annealed samples. To investigate the optical properties, the Fourier transform infrared (FTIR) transmission spectra of the as-grown and the annealed samples were recorded in the spectral region from 1000 cm^{-1} to 7000 cm^{-1}.

3. Results and discussion

The electrical properties of the as-grown and the annealed samples are summarized in Table 1. It is clear that the annealed samples have a decrease in carrier concentration. With the increase of the annealing temperature, a further reduction of the hole concentration is observed. Since the p-type conduction is caused by the native acceptor defects in undoped GaSb, the reduction of the hole concentration implies that the concentration of the acceptor defects decreases after the annealing treatment. To exclude the influence of impurities on the electrical conduction, the GaSb sample was analyzed by GDMS. The GDMS results of the annealed GaSb sample are summarized in Table 2. A total of 24 elements were analyzed in this measurement, including the most common metal and nonmetal elements. It is found that the concentrations of elements S and As have hardly any change at all compared with those in the as-grown sample (not listed in Table 2). For the other eight elements listed in Table 2, the concentrations are all below the detection limit. The other 14 metal elements are not detected by GDMS at all. Thus it can be concluded that the thermal annealing treatment does not bring in any new impurity. Through the analysis of the data in Table 2, it is clear that the improvement of the electrical property is not caused by the change of impurities in the samples. Thus, the decrease of the carrier concentration can be attributed to the reduction of the native defects in the samples.

Figure 1 shows the PL spectra of the GaSb samples obtained at 10 K. The spectra were collected by a Fourier transform infrared spectrometer (Bruker Vertex 80 V) with a spectral resolution of 0.5 meV in the step-scan mode. The PL was excited by the 647 nm Kr^{+} laser line together with a laser controller to warrant a stable excitation at 80 mW. The samples were cooled down by continuous flow liquid helium to about 10 K during the PL measurements. The luminescence signal was detected by a room temperature HgCdTe detector.

Table 1. Electrical properties of as-grown and annealed GaSb samples at 300 K.

Sample	Annealing temperature/°C	Resistivity /10^{-2} Ω·cm	Hall mobility /10^{2} $cm^2 \cdot V^{-1} \cdot S^{-1}$	Carrier concentration /10^{17} cm^{-3}
G95004-1	as-grown	6.519	6.419	1.584
	500	6.527	6.402	1.571
	550	6.883	6.054	1.415
	600	6.819	6.016	1.324
G95004-2	as-grown	6.760	6.382	1.464
	500	6.769	6.376	1.458
	550	6.794	6.311	1.407
	600	6.803	6.289	1.394

Table 2. GDMS result of annealed GaSb sample.

Element	Concentration/ppm	Element	Concentration/ppm
Na	< 0.001	Fe	< 0.005
AI	< 0.001	Cu	< 0.005
Si	< 0.001	Zn	< 0.005
P	< 0.001	As	0.08
S	0.004	Ga	matrix
K	< 0.05	Sb	matrix

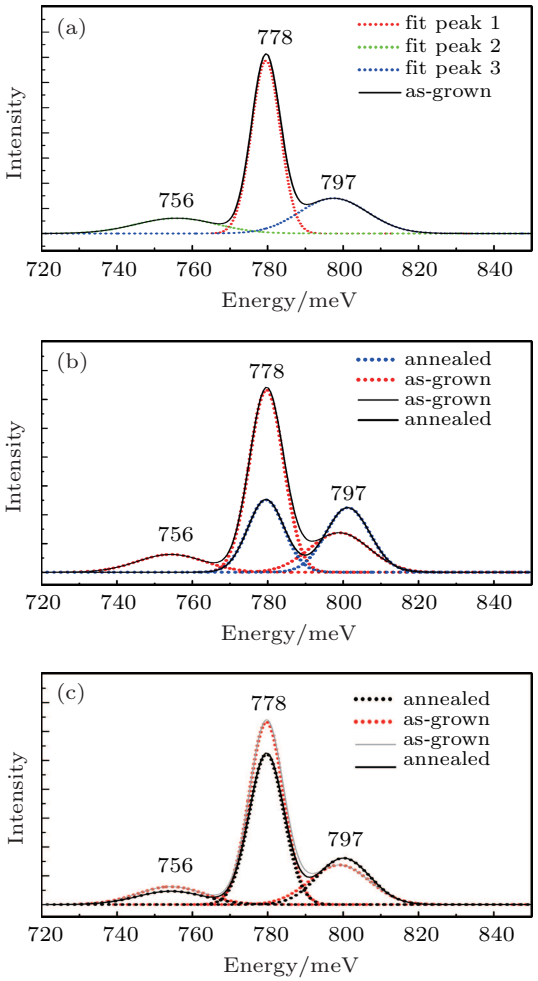


Fig. 1. (color online) PL spectra of undoped GaSb samples. (a) As-grown sample. Gaussian deconvolution of the spectrum reveals emission bands centered at 756 meV, 778 meV, and 797 meV (dashed lines). The solid line is the best-fit curve which corresponds to the experimental data. (b), (c) A comparison of as-grown and annealed samples. Gaussian deconvolution of the spectra recorded for the samples annealed at 500 °C (black dashed line), 550 °C (blue dashed lines), and as-grown sample (red dashed lines) is shown. Emission bands centered at 778 meV and 797 meV appear. The spectrum of the sample annealed at 600 °C has hardly any improvement compared to that of the sample annealed at 550 °C, thus it is not shown. The solid line is the best-fit curve which corresponds to the experimental data.

The low-temperature PL of the as-grown GaSb sample is dominated by recombination at the native acceptor (V_{Ga}) level via conduction band to bound acceptor (CA)[25] or donor acceptor (DA) pair transitions[26] located at 778 meV (∼1.594 μm), as shown in Fig. 1(a). The Gaussian deconvolution of the spectrum reveals two emission bands centered at 756 meV and 797 meV. The 756 meV peak is attributed to a transition from the conduction band to an acceptor center involving Ga_{Sb}.[27] The peak at 797 meV corresponds to a bound exciton, which is bound to the neutral acceptor level.[21] The 797 meV peak has been previously observed in liquid phase epitaxy (LPE) grown GaSb and dominates with a reduced native defect concentration.[28] Generally, the increase of the 797 meV peak indicates the decrease of the native defect concentration after annealing in antimony ambient. A comparison of the PL spectra of the as-grown and the annealed samples is given in Fig. 1(b). Although the PL spectrum is still dominated by the transition located at 778 meV, its intensity is apparently lower after the annealing treatment in ambient antimony. Besides, the 756 meV peak disappears completely in the PL spectrum of the annealed sample. The spectra in Fig. 1(c) have the same variation tendency as those in Fig. 1(b). However, the amplitude of the variation is not conspicuous, as the annealing temperature is relatively low.

It has been reported that p-type GaSb samples grown from Sb-rich solutions by liquid-phase epitaxy have lower hole concentrations.[21] The PL measurements on such samples have indicated that the native antisite defects related peaks are weak and their concentrations are reduced. It has also been reported that the intensity of the 756 meV transition increases upon annealing GaSb in Ga atmosphere.[29] From these observations, it is clear that the 756 meV peak is associated with Ga_{Sb}. The change of the above two peaks demonstrates that the concentrations of the two native acceptors V_{Ga} and Ga_{Sb} (associated with the 778 meV and 756 meV peaks, respectively) decrease, which is consistent with the decrease of the hole concentration illustrated in Table 1.

Naturally, it is believed that the structural rearrangement of Ga and Sb (as the main elements) and the change of the native defects (V_{Ga} and Ga_{Sb}) improve the properties of the annealed GaSb samples. As for the mechanism about the thermally induced transformation of the native defects, diffusion and migration behaviors of the Ga and Sb atoms in GaSb have to be considered.

Firstly, the influence of the in-diffusion of Sb atom is discussed. To estimate the in-diffusion depth of Sb in GaSb, Fick's second law can be used[30]

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}, \tag{1}$$

where D is the diffusion coefficient, C is the diffusion concentration, t is the diffusion time, and x is the diffusion distance. The diffusion coefficient of Sb in GaSb is computed with the constants and formula described in Refs. [31] and [32]. The Sb diffusion coefficient is extremely small, close to 10^{-19} $cm^2 \cdot s^{-1}$. The Ga diffusion coefficient, almost 10^{-17} $cm^2 \cdot s^{-1}$, is much larger than that of Sb under the same

diffusion condition.[33] The annealing time used in the calculation is 100 h. The diffusion length is calculated to be of the order of 10^{-7} m, it is very small compared with the thickness of the sample. As shown in Fig. 2, the diffusion concentration decreases rapidly with the increase of the diffusion depth. In the diffused layer, the diffusion concentration is very low. Thus, the in-diffusion of Sb from the annealing atmosphere is negligible and has little impact on the internal atomic migration of the annealed sample. However, the thermal annealing affects the self-diffusion inside the GaSb crystal and the quantity of the native acceptor defects in the GaSb sample. Since the Ga atom has a larger self-diffusion coefficient, it migrates more easily in the GaSb lattice upon thermal annealing. In this case, the Ga atom in antimony site (Ga_{Sb}) most likely moves to the gallium vacancy (V_{Ga}) site, resulting in a reduction of the concentration of native acceptor defects (V_{Ga} and Ga_{Sb}) and the formation of antimony vacancies (V_{Sb}).[34–36] This process can be described by the following reactions:

$$V_{Ga} + Ga_{Sb} \rightleftharpoons Ga_{Ga} + V_{Sb}, \quad (2)$$

$$V_{Sb} + Sb_i \rightleftharpoons Sb_{Sb}, \quad (3)$$

where Sb, Ga, and V are an Sb atom, a Ga atom, and a vacancy, respectively, and the subscripts show atomic sites and interstitial sites. It is noted that the in-diffusion of Sb is negligible and the as-grown GaSb is basically Ga-rich. The defect reaction leads to the decrease of the concentrations of the native defects (V_{Ga} and Ga_{Sb}) and the formation of V_{Sb}.

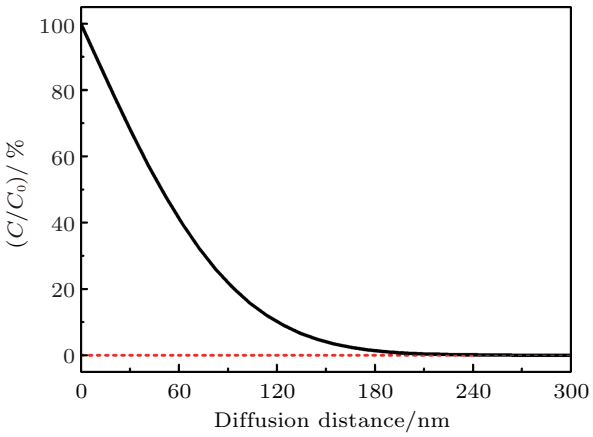


Fig. 2. (color online) The diffusion concentration of Sb atom changed along with the diffusion distance in GaSb sample, where C_0 is the diffusion concentration at the surface of the sample, and C is the diffusion concentration at a certain depth in the diffused layer.

Since V_{Sb} is usually a donor defect, it will increase the electrical compensation in the annealed p-type GaSb. Indeed, it is noted that the Hall mobility of the annealed GaSb samples decreases although the hole concentration decreases after the annealing. This is an indication that the donor defect is formed in the annealed samples and the carrier scattering is enhanced correspondingly.

Figure 3 gives the FTIR transmission spectra of the as-grown and the annealed GaSb samples in the 1.43–8 μm spectral range taken in ambient atmosphere. The transmission spectra were obtained at 300 K by a Fourier transform infrared spectrometer (Perkin Elmer Instruments Co. Ltd) with a spectral resolution of 4 cm^{-1}. The near- and mid-IR transmission spectrum of the as-grown GaSb sample is depicted by the dashed line. The maximum of the transmittance is located at 2 μm with the transmittance of 23.4%. In comparison, the GaSb sample annealed at 500 °C has a slight change, while the sample annealed at 500°C (or 600°C) exhibits the higher transmittance than the as-grown sample from 1.7 μm to 7 μm, indicating a decrease of the below-gap absorption. It has been confirmed that the below-gap absorption is caused by the existence of the native acceptor defects.[18,19] Thus the reduction of the below-gap absorption implies the reduction of the concentration of the native acceptor defects in the annealed GaSb sample. This result is consistent with the results of Hall measurement and PL spectra. Thus, the thermal annealing treatment improves the optical property of the GaSb sample though the reduction of the native acceptor defects.

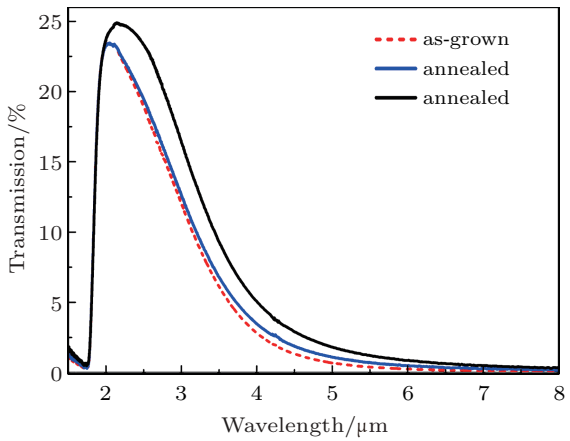


Fig. 3. (color online) Near- and mid-IR transmission spectra of undoped GaSb samples at 300 K taken in ambient atmosphere. The dashed line is the FTIR transmission spectrum of the as-grown GaSb sample. The blue and black lines correspond to the GaSb samples annealed at 500 °C and 550 °C, respectively. The spectrum of the sample annealed at 600 °C is almost coincident with that of the sample annealed at 550 °C, and is not shown here.

Since the GaSb substrates are not optically transparent in the regions of interest, the properties severely limit the performance of the optical devices grown on GaSb substrates. The existence of native acceptor defects in GaSb is exactly the key aspect that gives rise to the strong below gap absorption. The present result suggests a possible approach to improve the electrical and optical property of GaSb wafers and enable widespread application of GaSb wafers for long wavelength IR applications.

4. Conclusion

The p-type GaSb samples with lower background carrier concentrations have been obtained by a thermal annealing treatment. The Hall measurement and PL spectra confirm that the concentration of the native acceptors V_{Ga} and Ga_{Sb} in the sample decrease by annealing. Both the electrical property and the IR optical transmission of the GaSb single crystal are improved.

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