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OPTICAL AND ELECTRICAL PROPERTIES OF BULK GaSb AND AlGaSb†

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Optical measurements of bulk GaSb:S reveal the structure of the lattice two phonon absorption and acceptor-valence band transitions. A sulphur related local vibrational modes and several bands related to the optical transitions from the ground state of the acceptor level are observed. A comparison of transport and optical measurements for GaSb:Te and AlGaSb:Te shows that in the alloy it is easier to obtain high concentrations of the electrically active Te impurity.

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Recently, GaSb and its alloys have got an increasing importance as materials for optoelectronics. Heterostructure lasers for 1.5–2 μm wavelength range and photodetectors consisting of GaSb/AlGaSb or GaSb/AlGaAsSb layers are extensively developed [1]. It is therefore a bit surprising how little is known about optical properties of GaSb or AlGaSb compared to, e.g., GaAs or AlGaAs. For example, there have been no optical measurements of lattice or local vibrational modes carried out since the low resolution measurements in the fifties [2].

We hope that the unique growth technology of liquid phase electroepitaxy (LPEE) will help to bridge over this large gap between research and application especially when alloys are concerned. LPEE enabled us to obtain a set of thick (400–900 μm) samples of GaSb and AlGaSb with a high crystal quality and compositional uniformity. Such thick and large area samples are not attainable with the use of nonequilibrium growth techniques such as molecular beam epitaxy or even traditional Czochralski growth.

In our paper we present optical measurements of GaSb and AlGaSb doped with sulphur and tellurium carried out in wide spectral range (200–5000 cm^{-1}). A two phonon mode lattice absorption has been measured for GaSb and a new classification of phonon frequencies is attempted. In compensated *p*-type GaSb:S samples a strong broad absorption band is observed. It is tentatively attributed to the photoionization of the second charge state of the native double acceptor.

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In our study the GaSb:S bulk samples were grown by two different techniques: Czochralski and LPEE. The carrier concentration ranges from $p = 1 \times 10^{17}$ cm^{-3} to $n = 2 \times 10^{16}$ cm^{-3} at room temperature. It was not possible to obtain higher n-type carrier concentrations in GaSb:S although dopings either with very high amounts of sulphur or Ga_2S were attempted. The carrier mobilities are of the order of 300 cm^2/(V s) at room temperature and 900 cm^2/(V s) at 77 K in either p or n-type samples. The free carrier concentrations fall by one order of magnitude at lower temperatures (10–77 K) regardless of the room temperature initial carrier concentration or the type of conductivity.

Due to this free carrier "freeze out" process at lower temperatures the GaSb:S samples are perfectly suited for optical measurements. The absorption coefficient of GaSb:S was measured in the 200–5000 cm^{-1} wave number range with FTIR Bomem DA3 spectrometer at temperatures between 10 and 300 K and resolution of 2 cm^{-1}. Interesting features appear below 1000 cm^{-1} (Fig. 1). In both n-type and p-type samples strong lattice absorption bands can be observed in the 200–480 cm^{-1} spectral region. Their temperature dependencies suggest that all peaks above the strong restrahlen band centered at 230 cm^{-1} can be attributed to several two phonon summation bands. Due to the sufficiently high spectral resolution it was possible to reveal the detailed structure of this absorption. The results are summarized in Table.

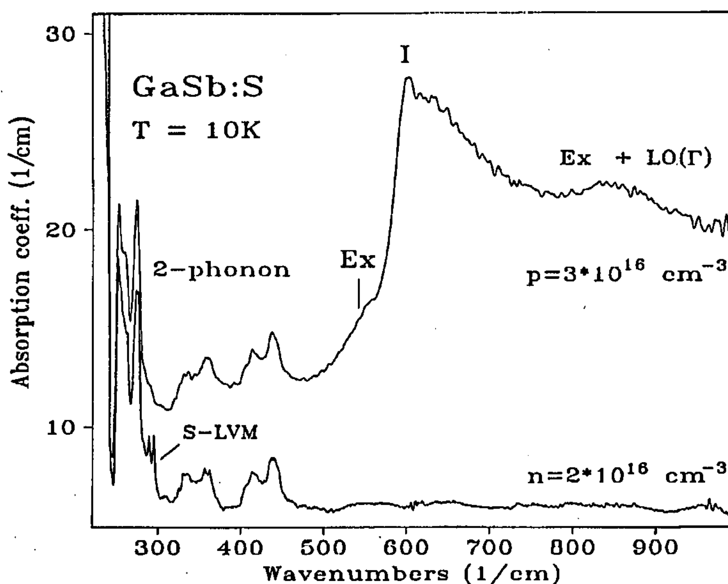

Fig. 1. Absorption bands in GaSb:S. In the n- and p-type samples two phonon absorption is seen. In the p-type sample acceptor optical transitions to the excited states (Ex), a photoionization band (I) and transition to a virtual state (Ex+LO(Γ)) are observed. In the n-type sample the sulphur related LVM appears.

TABLE

Assignment of the two phonon absorption bands in GaSb:S.

IR-Exp. This work	Assignment This work		Assignment acc. to neutron scatt. data [4]		Phonons at critical points	This work	Neutron scatt. [4]
252.3	252.0	LO(L)+TA(L)	250.6	LO(L)+TA(L)	TO(X)	220.5	212.0
255.3					LO(X)	216.5	211.7
260.0	260.0	2LA(L)	261.6	TO(L)+TA(L)	TA(X)	56.0	56.6
263.0	262.0	TO(L)+TA(L)			LA(X)	141.0	166.3
273.0	272.5	LO(X)+TA(X)	268.3	LO(X)+TA(X)	TO(L)	213.0	216.0
276.0	276.5	TO(X)+TA(X)	268.6	TO(X)+TA(X)	LO(L)	203.0	205.0
	282.0	2LA(X) forb.	306.6	2LA(L)	TA(L)	49.0	45.6
330.0			332.6	2LA(X) forb.	LA(L)	130.0	153.3
334.0	333.0	LO(L)+LA(L)					
337.0							
338–350	343.0	TO(L)+LA(L)					
356.0	357.5	LO(X)+LA(X)	358.3	LO(L)+LA(L)			
362.0	361.5	TO(X)+LA(X)	369.3	TO(L)+LA(L)			
406.5	406	2LO(L)					
413.0			410.0	2LO(L)			
418.0	416	TO(L)+LO(L)	421.0	TO(L)+LO(L)			
420–433	426.0	2TO(L)	423.4	2LO(X) forb.			
	433.0	2LO(X) forb.	423.7	TO(X)+LO(X)			
			424.0	2TO(X)			
435.0	437.0	TO(X)+LO(X)	432	2TO(L)			
440.0	441.0	2TO(X)					

If an identification of the bands is attempted, according to phonon Brillouin zone critical point analysis [3], one obtains the LA(X) and LA(L) phonon frequencies considerably lower than those obtained from the neutron diffraction experiments (i.e. 141 vs. 166 cm^{-1} and 131 vs. 155 cm^{-1}, respectively) [4]. Therefore, it seems to us that more detailed theoretical calculations are needed as the two phonon density of states does not necessarily originate from simple combinations of the one phonon densities at critical points but from regions of lower symmetry [5].

In the n-type and in the strongly compensated p-type GaSb:S two peaks at 289 cm^{-1} and 295 cm^{-1} appear. The strength of these peaks scales with the sulphur content. According to their temperature dependence they are attributed to local vibrational modes (LVM) of a sulphur related defect of probably C_s symmetry. To our knowledge it is the first observation of group VI element LVM in GaSb.

Above 500 cm^{-1} there is a strong electronic absorption in the p-type samples, which we attribute to a photoionization of the second charge state level of the Ga_{Sb} native double acceptor [6]. The structure seen on this broad band is similar to other acceptor photoionization bands seen in III–V compounds [7]. The maximum at 602 cm^{-1} corresponds to the photoionization itself. The small bump ($\nu = 547$ cm^{-1}) at the maximum lower energy side can be related to a strongly

concentration broadened excited state transition. The binding energy of the acceptor centre estimated from the photoionization band should be of the order of 75 meV which is in agreement with the Hall data [6].

At the higher energy side of the photoionization maximum there is another band ($\nu \approx 850\ \text{cm}^{-1}$) which, similarly to the acceptor absorption in GaAs or Ge [7], can be tentatively attributed to either a transition to the spin–orbit split valence band maximum or a virtual state consisting of the excited acceptor state plus the LO(Γ) phonon. The spin–orbit splitting in GaSb estimated from the first transition would be of the order of 30 meV which is quite improbable for an antimony-based compound [8]. Thus, the second transition has to be chosen for the origin of the 850 cm^{-1} band.

Tellurium incorporates into GaSb much easier than sulphur. The GaSb:Te and $Al_{0.2}Ga_{0.8}Sb$:Te crystals are n-type and have the dopant concentrations in the range of $5 \times 10^{17} - 2 \times 10^{18}\ \text{cm}^{-3}$. The carrier mobilities are orders of magnitude better than in the case of GaSb:S. We obtained for GaSb:Te $\mu_H = 5300\ \text{cm}^2/(\text{V s})$ at $T = 77$ K and 3400 $\text{cm}^2/(\text{V s})$ at $T = 300$ K. If tellurium is introduced into the GaSb and AlGaSb solutions in the same amounts then the concentration of electrically active centres is larger by almost an order of magnitude in the latter case. Probably the crystal alloying process reduces the native acceptor concentration in the compound. On the other hand, it is very difficult to obtain compensated or moderately doped GaSb:Te or AlGaSb:Te. In these samples the free carrier absorption makes impossible to carry out any optical measurements at wave numbers lower than 1000 cm^{-1}.

In conclusion, the new results on a relatively "unknown" III–V compound — GaSb are obtained. The two phonon absorption frequencies are measured with the resolution which makes possible the exact theoretical line assignment. Several optical transitions from the ground state of the Ga_{Sb} A^{-}/A^{--}-level are observed. LVM of a group VI element-related defect in GaSb are reported for the first time.

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References

[1] Y. Ohmori, Y. Suzuki, H. Okamoto, *Jpn. J. Appl. Phys.* **24**, L657 (1985); T. Miyazawa, S. Tarucha, Y. Ohmori, Y. Suzuki, H. Okamoto, *Jpn. J. Appl. Phys.* **25**, L200 (1986).

[2] H.J. Hrostowski, C.S. Fuller, *J. Phys. Chem. Solids* **4**, 155 (1958).

[3] J.L. Birman, *Phys. Rev.* **131**, 1489 (1963).

[4] M.K. Farr, J.G. Taylor, S. K. Sinha, *Phys. Rev. B* **11**, 1587 (1975).

[5] E.S. Koteles, W.R. Datars, *Can. J. Phys.* **54**, 1676 (1976).

[6] K. Nakashima, *Jpn. J. Appl. Phys.* **20**, 1085 (1981).

[7] R.A. Chapman, W.G. Hutchinson, *Phys. Rev. Lett.* **18**, 443 (1967).

[8] J.R. Chelikowsky, M.L. Cohen, *Phys. Rev. B* **14**, 556 (1976).